THEORY OF HEAT

Being Volume V of
"INTRODUCTION TO THEORETICAL PHYSICS"

BY

MAX PLANCK

Nobel Laureate, Foreign Member Royal Society, Professor of Theoretical Physics, University of Berlin, and President of the Kaiser Wilhelm Research Institute.

TRANSLATED BY

HENRY L. BROSE,
M.A., D.Phil. (Oxon.), D.Sc.
Lancashire-Spencer Professor of Physics,
University College, Nottingham.

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PREFACE

The present volume is the fifth and last of Professor Planck's series on Theoretical Physics. His reasons for treating the theory of heat at the end are based on the idea of systematization which characterizes the whole work. His method of presentation shows clearly that the theory of heat can be erected on the foundations of mechanics and electrodynamics (cf. p. 223), but that the converse is *not* possible. As previously, references to other volumes are made by means of Roman numerals, thus I refers to the volume on General Mechanics, II to that on the Mechanics of Deformable Bodies, III to that on the Theory of Electricity, IV to that on the Theory of Light. For example, on p. 89 of the present volume the reference II (284) stands for equation (284) of volume II (" Mechanics of Deformable Bodies ").

It is hardly necessary to mention that some of the most important developments of the theory of heat are due to Professor Planck's own brilliant researches, which have become classics in the history of physical thought. The idea of quanta of radiation, introduced at the dawn of the present century, has played a dominant part in physical theory up to the present time. Its significance is such that all efforts to construct a unitary field theory of physical phenomena—that is, a theory which would bring gravitational and electrodynamic events under a single scheme of laws—are doomed to failure unless a quantum assumption is included as an inherent part of the theory from the outset, as was recently remarked by Einstein in his Rouse Ball lecture at Cambridge (May 6, 1932).

To explain Professor Planck's procedure in the present volume reference must be made to some of the terms used in the earlier sections. In § 14 the author introduces the term "equivalent weights," which is followed by a definition of the term "molar weight" (gramme molecular weight, *Molgewicht*) and molar number (*Molzahl*) on p. 20. There is a certain unfamiliarity, however, to the English reader in the term *Molatom* (p. 23) since the term "gramme atom" has not come into common use. As the author reminds the reader at the top of p. 223, the weights of moles are standardized by convention, and it is only when we come to deal with "microscopic" as opposed to "macroscopic" conditions that it becomes necessary to introduce the idea of atoms and molecules; for example, to lead up to a discussion of thermodynamic probability (p. 222). Atomicity plays no part in the earlier sections. I have therefore considered it advisable to adhere closely to the German terminology even if the expression "molar atom" (gramme atomic weight, gramme atom) appears at first sight to contain a contradiction in terms. Other words which I have found it useful to introduce are: isochoric (or isosteric) on p. 10, isopiestic, also on p. 10, and enthalpy on p. 48. The term ergodic hypothesis (p. 229) has already appeared elsewhere in English. A more detailed explanation of this hypothesis is to be found in Berliner and Scheel's *Wörterbuch der Physik*.

Pains have been taken to make the English rendering as clear as possible, consistent with accurate translation, and it is hoped that any reader who may detect faults will kindly bring them to the attention of the translator.

My thanks are due to Mr. N. Davy, M.Sc., and Mr. E. H. Saayman, M.A., B.Sc., for carefully reading the proofs, and to Mr. C. N. Hinshelwood, M.A., F.R.S., Fellow of Trinity College, Oxford, for some helpful suggestions.

HENRY L. BROSE.

University College, Nottingham,
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INTRODUCTION

§ 1. The concept of heat, like all other physical concepts, originates in a sense-perception, but it acquires its physical significance only on the basis of a complete separation of the events in the sense-organs from the external events which excite the sensation. So heat, regarded physically, has no more to do with the sense of hotness than colour, in the physical sense, has to do with the perception of colour.

The external events that excite our thermal sense are manifold in their variety. They may have their seat either in material bodies with which we come into contact, or they may consist of electromagnetic waves which impinge on our organs of sense. According as the case may be, then, we speak of the heat in bodies or of radiant heat. These two types are quite different and are in general independent of each other. For example, very intense radiant heat can propagate itself through very cold air without heating the air to the slightest degree. We shall treat these two kinds of heat in succession.

As a starting point we here, as in the case of electricity, again choose the only trustworthy foundation on which we can build a new structure, namely, the Principle of the Conservation of Energy. This is usually called the First Law of Thermodynamics in the theory of heat. This principle forms the link between heat theory and mechanics and so serves as a basis for what is called Thermodynamics.

§ 2. But the Principle of the Conservation of Energy does not in itself suffice for building up a complete theory of heat. This is rendered possible only by adducing another principle, the Second Law of Thermodynamics, the content of which depends on a special peculiarity of thermal processes which distinguishes them in a characteristic way from mechanical and electromagnetic processes, and which, therefore, places the theory of heat in a special position as compared with other physical theories. That is also the reason why the treatment of the theory of heat forms the concluding volume of the present work.

For, let us imagine any (not too small) physical configuration, that is, any bodies in any electromagnetic field, which is completely cut off from its surroundings, so that the energy of the configuration remains constant (I, § 120). Within this configuration certain events will then occur the course of which is uniquely determined if we start out from a definite initial state. The following phenomenon then manifests itself. So long as only the laws of mechanics and electrodynamics are assumed to hold, the events will never come to an end and will retain their character for all time. Indeed, it may be proved that a state which has once existed can in the course of time occur any number of times again, if not in absolutely exactly the same way, at least to any desired degree of approximation (cf. § 131 below). But as soon as heat—no matter whether it be heat contained in bodies or radiant heat—enters into the question in any way the sequence of events finally, even if only asymptotically, approaches a definite end, in that the configuration tends to a state in which every mechanical or thermal change has ceased in the macroscopic sense (§ 115); this state is therefore called the state of thermal equilibrium. Hence all occurrences in which heat plays a part are in a certain sense unidirectional, in contrast with mechanical and electromagnetic events, which can equally well take place in the reverse direction, since for them the sign of the time factor is of no consequence. The essential feature of the second law of thermodynamics is that it furnishes a numerical criterion for the direction of the changes that occur in physical nature (§ 47).

In the first two parts of this book we shall deal with the heat in bodies, and afterwards, from the third part onwards, also with radiant heat.

PART ONE

THERMODYNAMICS

CHAPTER I

TEMPERATURE. MOLAR WEIGHT

§ 3. The first requirement of a theory of heat consists in defining in numerical terms the thermal state of a body concerning which our sensation when touching the body gives us only very imperfect information. To accomplish this we may make use of the experience that every body, if kept at constant pressure (say atmospheric pressure), changes its volume when heated, and so we can define the thermal state of a body by the amount of its volume at a particular instant. Instead of this, however, we may, to define its thermal state, also adduce any other property of the body which depends on the thermal state, for example, its thermo-electric e.m.f. or its galvanic resistance.

To be able to compare the thermal states of two different bodies numerically we require a further law derived from experience, which represents a special case of the general principle discussed in § 2 and which runs as follows : if two or more bodies (at rest) exert a thermal action on each other then, in contradistinction to mutual mechanical or electromagnetic actions, a state of thermal equilibrium always establishes itself, in which all change ceases. Using an expression which has been borrowed from mechanics, we then say that the bodies are in thermal equilibrium.

From this there immediately follows the important theorem : if a body *A* is in thermal equilibrium with two other bodies *B* and *C*, then *B* and *C* are themselves also in thermal equilibrium with each other. For if we make the bodies *A*, *B* and *C* form a connected ring so that each of the three bodies makes contact with the other two, then, by our assumption, thermal equilibrium also exists at the contact of (AB) as well as at that of (AC), and consequently also at the points of contact of (BC). For otherwise no general thermal equilibrium would be possible at all and this would contradict the principle above laid down.

The fact that this theorem is by no means obvious can be recognized particularly clearly if we apply it to the question of electrical equilibrium, for which it does not hold. For if we bring a copper rod which is in ~~electrical~~ equilibrium with dilute sulphuric acid into contact with a zinc rod which is in electrical equilibrium with the same sulphuric acid, equilibrium does not exist at the point of contact, but rather electricity flows from the copper to the zinc.

§ 4. It is because the above law holds for heat that we are able to compare the thermal states of any two bodies B and C with each other without bringing them into direct contact. We need only bring each body individually into contact with the arbitrarily chosen body A, which serves as a measuring instrument (for example, a quantity of mercury ending in a narrow tube), and define its thermal state by the prevailing volume of A, or still more appositely by the difference between this volume and some arbitrarily fixed " normal volume," namely, that volume which the body A occupies when it is in thermal equilibrium with melting ice. If the unit of this volume difference is chosen so that 100 is indicated when A is in thermal equilibrium with the steam of boiling water under atmospheric pressure, then it is called the *temperature* θ (in degrees Centigrade) with respect to the body A regarded as the thermometric substance. Two bodies at the same temperature are thus always in thermal equilibrium, and conversely.

§ 5. The temperature data of two different thermometric substances in general never agree except at 0° and 100°. Hence, to complete the definition of temperature there is no alternative but to make an expedient choice from among all substances and to use one of them to define the conventional temperature θ. It suggests itself to choose a gas for this purpose, since different gases, particularly at low densities, exhibit a very approximate agreement in their temperature data over a considerable range of temperature when used as thermometric substances. Even the absolute value of their expansion is almost the same for all gases, in so far as equal volumes when equally heated expand by the same amount, the pressure being assumed constant. The amount of this expansion is $\frac{1}{273 \cdot 2}$ of the volume for the temperature rise from 0° C. to 1° C. In the sequel we shall therefore refer the temperature θ to the gas thermometer, in particular to the hydrogen thermometer.

In spite of the advantages mentioned the temperature θ here introduced has in principle only a conventional and provisional significance. On the basis of the second law of thermodynamics we shall later, however, find it possible to define the so-called absolute temperature (§ 45) to which a real objective significance may be attached in so far as it is quite independent of the mechanical or electrical properties of individual bodies.

§ 6. In the following pages we shall occupy ourselves principally with homogeneous isotropic bodies of arbitrary shape, which have a uniform temperature and density in their interior and are subject to a uniform pressure acting everywhere normally to their surfaces and consequently themselves exert the same pressure outwards [cf. II (211)]. We shall take no account of surface phenomena. The state of such a body is determined by its chemical nature, its mass M, its volume V and its temperature θ. Thus all other properties of the state are dependent in a definite way on those just given; above all, the pressure p and the energy E depend on them. We shall discuss the former property in the present chapter and the latter in the next.

Since the pressure of a body clearly depends only on its internal constitution but not on its external shape and its mass, it follows that, besides depending on the temperature θ, the quantity p depends only on the *ratio* of the mass M to the volume V, that is, on the density or, respectively, on the inverse ratio, the volume of unit mass :

$$\frac{V}{M} = v \quad . \quad . \quad . \tag{1}$$

which, following accepted usage, we call the specific volume of the body. So there exists a definite relationship, characteristic of every substance :

$$p = f(v, \theta) \quad . \quad . \quad . \quad . \quad . \quad . \tag{2}$$

which is called the *equation of state* of the substance. The function f is always positive for gases; for liquid and solid substances it may also have negative values in some circumstances.

§ 7. The equation of state assumes its simplest form in the case of gases when their density is not too great. For by II (285) we have :

$$p = \frac{\Theta}{v} \tag{3}$$

where Θ depends only on the chemical nature of the gas and on the temperature θ (Boyle's Law, also known on the Continent as the Law of Boyle and Mariotte). On the other hand, by the definition of § 4, the temperature θ is proportional to the difference between the volume v and the "normal volume" v_0, that is :

$$\theta = (v - v_0) \, . \, P \quad . \quad . \quad . \quad . \tag{4}$$

where P depends only on the pressure p. Accordingly we have by (3) :

$$v_0 = \frac{\Theta_0}{p} \quad . \tag{5}$$

if Θ_0 denotes the value which the temperature function Θ assumes for $\theta = 0$.

Finally we use the empirical fact also introduced above in § 5, that the amount of the expansion for an increase of temperature from 0° to 1° is almost the same fraction:

$$\frac{1}{273 \cdot 2} = 0 \cdot 00366 = \alpha \qquad (6)$$

of the volume at 0° (Law of Gay-Lussac). Thus if we set $\theta = 1$, then $v - v_0 = \alpha v_0$, and equation (4) becomes:

$$1 = \alpha v_0 \, . \, P \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

By eliminating p, P, v_0 and v from the equations (3), (4), (5) and (7) we get the temperature function:

$$\Theta = \Theta_0 \, (1 + \alpha\theta) \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where now the constant Θ_0 depends only on the chemical nature of the gas. If we designate it by C, the equation of state (3) of a gas assumes the form:

$$p = \frac{C}{v}(1 + \alpha\theta) = \frac{CM}{V}(1 + \alpha\theta) \ . \qquad (9)$$

The numerical value of C is determined, as soon as the specific volume v of the gas is known, for any pair of values of θ and p, for example, 0° and atmospheric pressure; the values of C for different gases at the same temperature and under the same pressure are then obviously in the same ratio as the specific volumes v, or inversely as the densities, $\frac{1}{v}$. We may therefore say: at the same temperature and under the same pressure the densities of all gases bear perfectly definite ratios to one another. A gas is therefore often also characterized by the constant ratio of its density to the density of a normal gas at the same temperature and pressure (specific density with respect to air or hydrogen). Thus if we denote the quantities referred to hydrogen, for example, by means of a suffix H, the specific density of a gas with respect to hydrogen is:

$$\frac{1}{v} : \frac{1}{v_H} = \frac{C_H}{C} \qquad (10)$$

The following are the actual specific densities of various gases with respect to hydrogen: oxygen 16, nitrogen 14, air 14·4, water-vapour 9, ammonia 8·5, hydrogen peroxide 17.

§ 8. The equation of state (2) of a substance allows all questions concerning the behaviour of the substance with regard to arbitrary changes of temperature, volume and pressure to be answered completely. Attention must be paid to the way in which the quantities are chosen as independent and dependent variables. If, *first*, the pressure p is kept constant the changes are called isobaric or isopiestic. The term "volume coefficient of expansion" is then given to the ratio of the increase of volume for an increase of 1° to the volume at 0°, that is, to the quantity $\frac{V_{\theta+1} - V_\theta}{V_0}$. For a gas we have by the equation of state (9) that:

$$V_{\theta+1} - V_\theta = \frac{CM\alpha}{p} \quad \text{and} \quad V_0 = \frac{CM}{p},$$

so that the "volume coefficient of expansion" for all gases is equal to α. If, in the *second* place, the volume is kept constant we speak of isochoric or isosteric changes. The pressure coefficient of expansion is then the ratio of the increase of pressure for a temperature increase of 1° to the pressure at 0°, that is, the quantity $\frac{p_{\theta+1} - p_\theta}{p_0}$. For a gas we have by the equation of state (9) that $p_{\theta+1} - p_\theta = \frac{C\alpha}{v}$ and $p_0 = \frac{C}{v}$; thus the pressure coefficient of expansion for all gases likewise becomes equal to α. If, *thirdly*, the temperature is kept constant, the changes are called isothermal and the name "isothermal coefficient of elasticity" is given to the ratio of an infinitely small increase of the pressure to the resulting contraction per unit volume; thus it is the quantity:

$$\frac{dp}{-\frac{dV}{V}} = -\left(\frac{\partial p}{\partial v}\right)_\theta \cdot v.$$

For a gas we have, by the equation of state (9):

$$\left(\frac{\partial p}{\partial v}\right)_\theta = -\frac{C}{v^2}(1 + \alpha\theta)$$

and hence the coefficient of elasticity of the gas is $\frac{C}{v}(1 + \alpha\theta)$, that is, it is equal to the pressure p. The value of the reciprocal of the coefficient of elasticity is called the "coefficient of compressibility."

The three coefficients which characterize the behaviour of a substance in isobaric, isochoric and isothermal changes are not independent of one another, but are connected in the case of any arbitrary substance by a fixed relationship. For by differentiating the equation of state we get generally:

$$dp = \left(\frac{\partial p}{\partial \theta}\right)_v . d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta . dv$$

If we now set $dp = 0$, we obtain the relation which holds for an isobaric change between the differentials $d\theta$ and dv; expressed in corresponding notation this relation is:

$$\left(\frac{\partial v}{\partial \theta}\right)_p = -\frac{\left(\frac{\partial p}{\partial \theta}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_\theta} \qquad (11)$$

Accordingly, for every state of a body it is possible to calculate one of the three quantities, volume coefficient of expansion, pressure coefficient of expansion and coefficient of compressibility from the other two.

§ 9. **Gas Mixtures.** If different but arbitrarily great quantities of one and the same gas at the same temperature and pressure which are initially separated by partitions are suddenly brought into contact with one another by the removal of the partitions, the volume of the total system obviously remains equal to the sum of the separate volumes. Further, if the gases brought into contact are different in character, experiment shows that in this case too, provided the temperature is kept constant and uniform and the pressure is kept uniform, the total volume remains permanently equal to the sum of the originally separate volumes, although at the same time a slow process of mixing, diffusion, takes place which is ended only when the composition of the mixture in every part of the space occupied by the gases is the same, that is, when the mixture has become physically homogeneous.

We may regard the resulting mixture as constituted in one or other of two ways. *Either* we may assume that in the process of mixing each individual gas divides up into an enormously large number of small parts, each of which, however, retains its volume and its pressure, and that these small parts of the different gases mix together during diffusion without penetrating into one another. Then each individual gas would, after the completion of the diffusion process, still retain its old volume (partial volume) and all the individual gases would have the same common pressure. *Or else*—and this is the view which, as we shall later find (§ 12), can alone be justified—we may assume that the individual gases also change in the smallest parts of their volumes and inter-penetrate one another, so that when diffusion is completed each individual gas, so far as one may still speak of such, occupies the whole volume of the mixture and fills it uniformly densely. Then, corresponding to the resulting dilution, the pressure of the individual gas has sunk to a smaller value, that of its partial pressure.

If we denote the individual gases by numerical suffixes, while the volume V, the temperature θ and the pressure p of the mixture are written without a suffix, the partial volumes of the individual gases in the mixture are (if we adopt the first view), by (9):

$$V_1 = \frac{C_1 M_1}{p}(1 + \alpha\theta),\ V_2 = \frac{C_2 M_2}{p}(1 + \alpha\theta) \qquad (12)$$

where:

$$V_1 + V_2 + \ . \ . \ . \ = V \qquad (13)$$

and the partial pressures (if we take the second view) are :

$$p_1 = \frac{C_1 M_1}{V}(1 + \alpha\theta),\ p_2 = \frac{C_2 M_2}{V}(1 + \alpha\theta) \quad . \quad . \quad . \qquad (14)$$

By addition we have :

$$p_1 + p_2 + \ .\ .\ .\ = \frac{V_1}{V}\cdot p + \frac{V_2}{V}\cdot p + \ .\ .\ .\ = p \quad . \qquad (15)$$

which is Dalton's Law. It states that in a mixture of gases the pressure is equal to the sum of the partial pressures of all the individual component gases. We further see that :

$$p_1 : p_2 : \ .\ .\ .\ = C_1 M_1 : C_2 M_2 : \ .\ .\ .\ = V_1 : V_2 : \ .\ .\ . \qquad (16)$$

That is, the partial pressures, on the second view, are in the ratio of the partial volumes on the first view.

The composition of a gas-mixture is defined either by the ratios of the masses M_1, M_2, . . . or by the ratios [which, by (16), are constant] of the partial pressures or, respectively, by the partial volumes of the individual components. Accordingly we speak of either percentages by weight or percentages by volume. For example, atmospheric air contains about 23·1% of oxygen and 76·9% of nitrogen by weight but 20·9% of oxygen and 79·1% of nitrogen by volume.

The equation of state of a gas mixture is, by (12) and (13) :

$$p = \frac{C_1 M_1 + C_2 M_2 + \ .\ .\ .}{V}(1 + \alpha\theta) \quad . \qquad (17)$$

or :

$$p = \frac{C_1 M_1 + C_2 M_2 + \ .\ .\ .}{M}\cdot\frac{M}{V}(1 + \alpha\theta)$$

Thus it corresponds perfectly with the equation of state (9) of a simple gas whose characteristic constant is :

$$C = \frac{C_1 M_1 + C_2 M_2 + \ .\ .\ .}{M_1 + M_2 + \ .\ .\ .} \quad . \qquad (18)$$

Hence an investigation of the equation of state can never decide whether a gas is chemically simple or whether it is formed of a mixture of different simple gases.

§ 10. The equation of state (9) holds for all gases and vapours if their densities are sufficiently low. But if their densities exceed a certain order of magnitude certain deviations always occur and the equation of state must then be given a more general form. In the course of time a whole series of different equations of state has been given which fulfil their purpose more or less well. The first and simplest of them is due to van der Waals; it is of particular interest because it also applies to the liquid state. Van der Waals' equation runs:

$$p = \frac{C(1 + \alpha\theta)}{v - b} - \frac{a}{v^2} \quad . \quad . \quad (19)$$

where a and b are other constants which depend on the nature of the substance. For great values of v the equation reduces to (9), as it should do.

The functional dependence of the pressure p on the volume v and the temperature θ may be conveniently depicted by drawing "isothermal" curves; for any arbitrary constant temperature θ two associated values of v and p are plotted as abscissa and ordinate of a point in a plane. The complete family of all isothermals then gives a complete picture of the equation of state. By the equation of state (9) all isothermals are clearly rectangular hyperbolas which have the co-ordinate axes for their asymptotes. For $pv =$ const. holds for them. By van der Waals' equation (19), on the other hand, the isothermals assume quite different forms, whose character is indicated in Fig. 1. In general, as can be seen from (19), there are actually three values of v for each value of p. Hence an isothermal will in general be intersected at three points by a straight line parallel to the v-axis. But two of them may be imaginary, as actually occurs for high values of θ. At high temperatures (for example, θ' in the figure) there is thus for a given pressure only a single real volume, whereas at low temperatures (for example, θ in the figure) three real values of the volume correspond to a definite value of the pressure. Of these three values, represented in the figure, for example, by α, β, γ, only the smallest (α) and the greatest (γ) can signify a stable state of the substance, such as can be produced in physical nature. For in the case of the intermediate volume (β) the pressure along the isothermal clearly increases as the volume increases; that is, the compressibility is negative. Such a state is only of theoretical importance.

The point α corresponds to the liquid state; the point γ corresponds to the gaseous state at the temperature θ and at the pressure p represented by the common ordinate

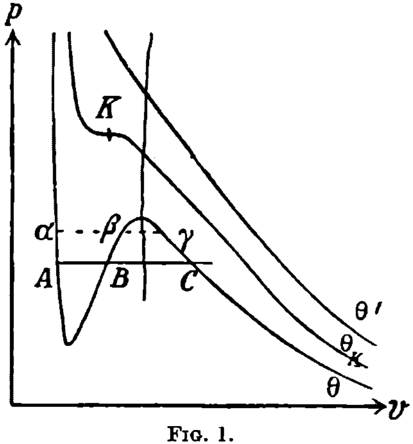

Fig. 1.

of α, β and γ. But, again, in general only one of these two states α and γ is stable (in the figure it is the state α). For if the gaseous substance, which, say, is enclosed in a cylinder with a movable piston, is compressed, the temperature θ being kept constant during the process, the successive states will be denoted in the first place by the points to the right on the isothermal θ. As the volume decreases the graph point moves continually further to the left along the isothermal until it reaches a perfectly definite point C. On further isothermal compression, however, the point does not go beyond C; rather the substance partially condenses, that is, it resolves into a liquid and a gaseous part which, of course, have a common pressure and temperature. If the isothermal compression is continued still further the state of the gaseous part is always denoted by the fixed point C, that of the liquid part accordingly always by the fixed point A of the same isothermal. The only change that occurs in the process is that more and more vapour is precipitated. C is called the saturation point of the gaseous substance at the temperature θ. Finally, when all the vapour has been condensed the whole substance is in the liquid state A and so again behaves homogeneously. Further isothermal compression then again leads to increase of density and of pressure along the isothermal θ, during which also the point α of the figure is passed through. The figure shows that on this side the isothermals are much steeper than on the other, that is, the compressibility is far less.

Sometimes, in compressing a vapour, the isothermals are successfully continued beyond the point C a certain distance towards γ and "super-saturated vapour" is produced. Only more or less unstable states of equilibrium are obtained, as may be recognized from the fact that very small disturbances of the equilibrium may be followed by sudden condensation, that is, by an abrupt transition to the stable state. Nevertheless the study of super-saturated vapours invests also the theoretical part of the isothermals with a certain practical importance.

§ 11. From the above remarks we see that every isothermal which admits of three real volumes for certain values of p has two definite points A and C which denote the condition of saturation. Their position cannot be directly read off from the graph of the isothermals. But the laws of thermodynamics lead to a simple geometrical construction for giving these points; this method is worked out in Chapter IV (§ 61). The higher we choose the temperature the more the region intercepted between the isothermal and the line parallel to the v-axis, which cuts it in three points, shrinks together, and the closer these three points approach one another. The transition to those isothermals which resemble hyperbolas and are cut by parallels to the v-axis in only one point is indicated by a definite isothermal for which the three previous points of intersection coincide. This point thus represents a point of inflexion of the isothermal in question, at which the tangent of inflexion runs parallel to the v-axis. It is the *critical point* K of the substance (see Fig. 1); it specifies the critical temperature θ_k, the critical volume v_k and the critical pressure p_k. At the critical point the saturated vapour becomes identical with its condensate. Above the critical temperature $(\theta > \theta_k)$ and above the critical pressure $(p > p_k)$ no condensation at all occurs, as is easily seen from the figure. From the figure we also learn directly that there is no definite boundary between the gaseous and the liquid state, as it is easy to pass from the region of definitely gaseous states, for example, from the point C, to a curve which passes over and around the critical point into the region of definitely liquid states, for example, to A, without anywhere encountering a saturated state. For this reason, too, we cannot in principle distinguish between gases and vapours.

The critical state may easily be calculated from the equation of state (2). For from the preceding observations we know that the following two equations hold for it:

$$\left(\frac{\partial p}{\partial v}\right)_\theta = 0 \text{ and } \left(\frac{\partial^2 p}{\partial v^2}\right)_\theta = 0 \qquad (20)$$

The first of these expresses that the tangent of the isothermal at K runs parallel to the v-axis; the second states that the isothermal has a point of inflexion at K.

For van der Waals' equation we have in particular:

$$v_k = 3b,\ \theta_k = \frac{1}{\alpha}\left(\frac{8a}{27bC} - 1\right),\ p_k = \frac{a}{27b^2}\,. \qquad (21)$$

§ 12. If two gases or vapours mix which have so great a density that the simple equation of state (9) no longer holds for them, it is possible by applying Dalton's Law to arrive at an expression which is very approximately valid for the equation of state of the mixture. This law states that the pressure of the mixture is equal to the sum of the partial pressures which each gas (or vapour) would exert if it alone filled the whole volume at the same temperature. This law also furnishes us with an answer to the question, which was left open above in § 9, as to whether we must ascribe to the individual components of a gas mixture a common pressure and different volumes or a common volume and different pressures. That the latter view is alone admissible follows from the consideration of a vapour whose temperature is below the critical temperature. For example, if we take a mixture of air and water vapour at 0° and at atmospheric pressure, it is impossible to assume the water vapour as being at the pressure of one atmosphere, as water vapour at 0° does not exist at all at this pressure. There is no course open, then, but to ascribe a common volume and different pressures to the air and the water vapour.

§ 13. Having dealt with the interdependence of the variables p, v and θ of the equation of state we shall next fix our attention on the significance of the constant C in the gas equation (9). Its value is dependent on the chemical constitution of the gas. What distinguishes chemical from physical events is above all the fact that the former in general occur discontinuously, spasmodically, whereas the latter in general occur continuously. For the chemical nature of a substance is something constant and between different constants no continuous transitions are possible, but only steps. Accordingly the different chemical substances do not form a uniform series connected by continuous transitions, but rather a discrete series in which the individual members are sharply differentiated from one another. This manifests itself in the experimental fact that in every chemical change the substances which are reacting with one another combine or dissociate in quite definite and constant proportions by weight. We may therefore ascribe to every chemically homogeneous substance, whether it be an element or a compound, a definite weight (more correctly mass), namely, its equivalent weight, as follows. We fix the equivalent weight arbitrarily for some particular substance, for example, 1 gramme, say, of hydrogen. We then find the chemically equivalent weight for another element, say oxygen, by ascertaining that weight of oxygen which combines chemically with 1 gramme of hydrogen to form water, namely, 8 grammes. The amount, by weight, of the resulting compound, 9 grammes, is then the equivalent weight of water. Proceeding in this way we easily arrive at the equivalent weight for all chemical substances, even for those elements which do not combine directly with hydrogen at all, since elements can always be found that combine both with the element in question as well as with hydrogen and so establish an indirect connexion.

This law of the constancy of equivalent weights impresses itself clearly on our minds if we regard the equivalent weight a of a substance as a definite single quantity, as a sort of individual. Every chemically homogeneous quantity of mass M then contains a definite number n of equivalent weights or equivalents :

$$n = \frac{M}{a} \quad . \qquad . \quad (22)$$

and the following law then holds : in every chemical change equal numbers of equivalent weights react with one another.

This definition, however, suffers from a defect which was seriously felt for a time in theoretical chemistry. It is due to the fact that two elements can often enter into combination in more than one way with each other, which makes the equivalent weight have more than one value. For example, 1 gramme of hydrogen combines not only with 8 grammes of oxygen to form water but also with 16 grammes of oxygen to form hydrogen peroxide, and there is no material reason for preferring the one compound to the other in defining the equivalent weight. But experiment shows that in such a case the different possible values of the equivalent weight always bear simple integral ratios to one another; thus in the case of oxygen just quoted $8 : 16 = 1 : 2$. So we must generalize the assertion that "equal" numbers of equivalents react with one another by stating that the equivalents react with one another in "simple integral proportions."

§ 14. This indefiniteness in the definition of the equivalent weight which we have just described is overcome in the case of gaseous substances by selecting from the different values that offer themselves for the equivalent weight a of a gas a definite value and calling it the *molar weight* m of the gas (cf. also end of § 115). This is rendered possible by the further experimental law that gases react not only, like all other substances, in accordance with simple equivalent numbers but also according to simple volume ratios, when taken at the same temperature and pressure (Gay-Lussac's Law). From this it follows immediately that the equivalent numbers n contained in equal volumes of different gases and defined by (22) bear simple integral ratios to one another. The values of these simple ratios are, of course, subject to the same uncertainty as the values of the equivalent weights a.

If we now make the last law more precise by defining that the equivalent numbers n contained in equal volumes of different gases and defined by (22) are *equal* to one another, this means that we are making a particular choice among the different values that come into question for the equivalent weight a, and in this way we obtain for every gas a perfectly definite molar weight m and likewise, by (22), for a given quantity M of a gas a definite molar number:

$$n = \frac{M}{m} \,. \tag{23}$$

Equal volumes of all gases under the same conditions of temperature and pressure contain the same numbers of moles (Avogadro's Law).

The definition of the molar weight m as a definite quantity dependent only on the nature of the gas itself and not on chemical reactions with other substances represents one of the most important and fruitful achievements of theoretical chemistry. It allows m to be measured by physical methods. For, since for any two gases 1 and 2 the numbers of moles n contained in equal volumes under the same conditions of temperature and pressure are the same, we have by (23) :

$$\frac{M_1}{m_1} = \frac{M_2}{m_2}.$$

That is, the molar weights m_1 and m_2 are in the ratio of the masses contained in equal volumes, namely $M_1 : M_2$, or in the ratio of the densities. Now, by § 7, the ratio of the densities of the two gases is represented by the constant ratio $\frac{1}{C_1} : \frac{1}{C_2}$. Accordingly we obtain :

$$m_1 : m_2 = \frac{1}{C_1} : \frac{1}{C_2} \quad . \qquad (24)$$

and so the molar weight can be calculated from the equation of state.

If we set the molar weight of hydrogen equal to m_H, the molar weight of any other gas is by (24) :

$$m = \frac{C_H}{C} \cdot m_H \quad . \qquad (25)$$

By (10) the factor $\frac{C_H}{C}$ is the specific density of the gas with respect to hydrogen; the value of the specific density is given at the end of § 7 for several gases.

§ 15. Having fixed the molar weight of any gas unambiguously by (25), we may now also give an equally definite answer to the further question as to how the molar weight of a chemical compound is composed of the molar weights of its chemical elements. Let m be the molar weight of a chemical compound which is formed by two chemical elements having the molar weights m_1 and m_2. The question is: how many moles of each element combine together to form a mole of the compound? We are to regard the molar weights m, m_1, m_2 as known, by (25), and we require to find the molar numbers n_1 and n_2.

To calculate these two unknowns we first have the equation:

$$n_1 m_1 + n_2 m_2 = m \quad . \quad . \quad . \quad (26)$$

and, secondly, the ratio of the weights of the two elements in the compound:

$$\frac{n_2 m_2}{n_1 m_1} = \frac{M_2}{M_1} \quad . \quad . \quad . \quad (27)$$

From these equations it follows that:

$$n_1 = \frac{m}{m_1\left(\frac{M_2}{M_1} + 1\right)} \quad . \quad (28)$$

$$n_2 = \frac{m}{m_2\left(\frac{M_1}{M_2} + 1\right)} \quad . \quad (29)$$

For example, for a mole of water vapour, consisting of hydrogen (1) and oxygen (2), we have $m_1 = m_H$. Further, by (25), taking into account the numerical values, given at the end of § 7, for the specific densities of oxygen and water vapour with respect to hydrogen, we have $m_2 = 16 m_H$, $m = 9 m_H$, and for the ratio of the weights we have $\frac{M_2}{M_1} = 8$.

Consequently, by (28) and (29):
$n_1 = 1$, $n_2 = \frac{1}{2}$; that is, a mole of water vapour consists of a mole of hydrogen and half a mole of oxygen.

For a mole of ammonia, consisting of hydrogen (1) and nitrogen (2) we have:

$$m_1 = m_H$$

Further, by (25) and § 7:

$$m_2 = 14 m_H, \; m = 8{\cdot}5 m_H$$

and for the ratio of the weights we have :

$$\frac{M_2}{M_1} = \frac{14}{3}$$

Consequently by (28) and (29):

$$n_1 = \frac{3}{2}, n_2 = \frac{1}{2}$$

That is, a mole of ammonia consists of one and a half moles of hydrogen and half a mole of nitrogen.

§ 16. The smallest amount by weight of a chemical element which occurs in the molecules of the compounds of the element is called an atom or, more accurately—to distinguish it from the true atom—a molar atom (cf. the remarks in the preface and in § 115). Hence half a mole of hydrogen is called a molar atom of hydrogen and denoted by H; half a mole of oxygen is called a molar atom of oxygen, O; half a mole of nitrogen is called a molar atom of nitrogen, N. Thus a mole of any of these elements consists of two molar atoms : H_2, O_2, N_2. In the case of mercury and the inert gases, on the other hand, the molar atom is equal to the whole mole, because none of their compounds contains fractions of a mole. The mole of water vapour is denoted by H_2O, that of ammonia by NH_3.

To arrive at definite numerical values for the molar atomic and molar weights it yet remains to fix in some arbitrary way the molar atomic weight of some one element chosen at random. Formerly H was set $= 1$ grm. and therefore $O = 16$ grms. But after it had been shown that the ratio of the molar weights of oxygen and hydrogen is not exactly equal to 16 but to 15·87, and in view of the fact that in the case of most elements the oxygen compounds have been much more accurately analysed than the hydrogen compounds, it has become customary to use the molar atomic weight of O as 16 for the purpose of definition. The molar weight of oxygen is then:

$$O_2 = 32 \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and the molar weight of hydrogen:

$$H_2 = m_H = \frac{32}{15{\cdot}87} = 2{\cdot}016 \quad . \quad . \quad . \quad (31)$$

and the molar atomic weight of hydrogen:

$$H = 1{\cdot}008 \quad . \quad . \quad . \quad . \quad (32)$$

In general the molar weight of a gaseous chemical compound is, by (25) and (31):

$$m = 2{\cdot}016 \cdot \frac{C_H}{C}$$

or, equivalently:

$$m = 32 \cdot \frac{C_0}{C}$$

if C_0 denotes the constant of the equation of state for oxygen.

Conversely, if the molar weight m of a gas is known, it is possible to give the value of the constant C of its equation of state (9):

$$C = \frac{2{\cdot}016 \, . \, C_H}{m} = \frac{32 \, . \, C_0}{m} \qquad (33)$$

Now the density of oxygen at 0° C. and atmospheric pressure is:

$$\frac{1}{v} = 0{\cdot}0014291 \text{ grm./cm.}^3$$

so that by (9), with $\theta = 0$ and $p = 1{,}013{,}250$ [grm. cm.$^{-1}$. sec.$^{-2}$], which is given in II (284), we have:

$$C_0 = pv = \frac{1013250}{0{\cdot}0014291} = 7{\cdot}09 \, . \, 10^8 \, [\text{cm.}^2 \, \text{sec.}^{-2}]$$

and, by (33), the equation of state (9) becomes:

$$p = \frac{2{\cdot}27 \, . \, 10^{10}}{mv}(1 + \alpha\theta) = \frac{2{\cdot}27 \, . \, 10^{10} \, . \, M}{mV}(1 + \alpha\theta) \quad . \quad (34)$$

But $\frac{M}{m}$ is the number of moles contained in the gas, namely n; therefore:

$$V = \frac{2{\cdot}27 \,.\, 10^{10}}{p} \cdot n \,.\, (1 + \alpha\theta) \qquad (35)$$

That is, the volume of a gas at a definite pressure p and definite temperature θ depends only on the number of moles it contains and not at all on the nature of the gas; and this is in conformity with Avogadro's Law.

Equation (35) also holds for a mixture of gases, that is, for the case when the n moles of a gas are not all of the same kind. This can be seen immediately from (17) if we replace the constants C_1, C_2, . . . in it by the corresponding molar weights m_1, m_2, . . . from (33) and if we reflect that the ratios $\frac{M_1}{m_1}$, $\frac{M_2}{m_2}$ . . . represent the numbers of moles n_1, n_2, . . . that occur in the gas. Simultaneously we get the result that the ratios (16) of the partial pressures or the partial volumes are no other than the ratios of the numbers of moles of the individual component gases of the mixture:

$$p_1 : p_2 : \ldots = n_1 : n_2 : \ldots \qquad (36)$$

If, accordingly, the equation of state of a mixture of gases differs in no way from the equation of state of a chemically homogeneous gas we cannot speak of a definite molar weight of the mixture but only of a "mean" molar weight, that is, of that molar weight which a chemically homogeneous gas would have if it contained the same number of moles in the same mass as the mixture. Thus:

$$\frac{M_1 + M_2 + \ldots}{m} = \frac{M_1}{m_1} + \frac{M_2}{m_2} + \ldots \qquad (37)$$

From this we can calculate the mean molar weight of the mixture. In the case of atmospheric air, for example, the mean molar weight is 28·8, which corresponds with the value given for the specific density of air at the end of § 7.

§ 17. Up to this point of the discussion we have assumed that the gas under consideration satisfies the equation of state (9). For in the equation (35) the number of moles n is then a constant quantity independent of the pressure and the temperature. But if a gas or a vapour manifests a behaviour which deviates from that expressed by this equation of state we are faced with the alternative of applying a generalized equation of state, such as that of van der Waals, or else of retaining equation (35) and assuming a value for the number of moles n which is dependent on the temperature and the pressure: in other words, to regard as the cause of the deviation from the equation of state (9) either physical or chemical circumstances. According to the first view the moles of the gas remain unchanged but they act on one another in a complicated manner, while on the second view the gas forms a mixture of variable percentages whose constituents individually satisfy the equation of state (9). The percentage content may then be calculated by (26) for every temperature and every pressure from the mean molar weight $m = \frac{M}{n}$, corresponding to the number of moles n, if the molar weights m_1, m_2, of the constituents are known. This view is found to be most fruitful in the cases where very considerable changes of the specific density are involved, that is, in the case of the so-called abnormal vapour densities; it applies particularly when the specific density beyond a certain range of temperature or pressure again becomes constant. For then the chemical transformation has been completed and the molar constituents no longer change. For example, amyl bromide satisfies the gas equation (9) both below 160° C. as well as above 360° C., but in the latter state it has only half the density, that is, double the number of moles, corresponding to the transformation:

$$C_5H_{11}Br = C_5H_{10} + HBr$$

But if the deviations from the equation of state (9) are unimportant they are usually ascribed to physical causes and are regarded as heralding condensation. A fundamental separation of the chemical influences from the physical influences which would complete the definition of molar weight for variable specific densities cannot be given from the standpoint of pure thermodynamics. In general, therefore, physical as well as chemical changes will have to be considered as causes for these deviations from the equation of state (9). All that we may state with certainty is that when the density becomes less the physical influences become progressively less important compared with the chemical influences. For when the density is sufficiently small the equation of state (9) holds for all gases and vapours of constant chemical composition.

CHAPTER II

FIRST LAW OF THERMODYNAMICS

§ 18. THE first law of thermodynamics is no other than the universal Principle of Conservation of Energy applied to heat processes. The energy E of a physical configuration may be regarded as a "capacity" to do work (I, § 49) which is conditioned and uniquely determined by the momentary state of the configuration, and which can occur in various forms and undergo various transformations but, so long as the configuration is isolated from the exterior, is of definite amount which does not vary with respect to the time: thus $E =$ const. or $E' - E = 0$ if E refers to the initial state and E' to the final state of the configuration.

So soon as the configuration is subjected to influences from without or exerts an action on the outside its energy E alters according to the measure of this external action. If the external action is of a mechanical nature the change of energy is equal to the work A which the external forces perform on the material points of the configuration or system (I, § 120). If the external action is electromagnetic by nature the change of energy is equal to the Poynting energy-flux P (III, § 4) directed inwards through the surface of the system. If, finally, the external action is of a thermal nature the energy change is equal to the quantity of heat Q which has *passed from without into* the system.

For the general case when all three kinds of external effects are to be taken into consideration we thus obtain as the expression for the principle of the conservation of energy:

$$E' - E = A + P + Q\,. \tag{38}$$

The sum on the right-hand side is called the *mechanical equivalent of the external effects* which are produced on the configuration during its transition from the initial state to the final state.

This equation must not be regarded as being only a definition. For its validity depends on an assumption which is not self-evident and which can be justified only by experiment. This assumption is that the value of the energy E is to be taken as determined by the momentary state of the system. Thus if a physical system is allowed to pass in several ways or, as it is often expressed, along different routes from a definite initial state to a definite final state, the mechanical equivalent of the external actions must every time lead to the same value. This law is not self-evident but may be tested by measurements in an infinite number of ways. If it were found to be transgressed in one single instance, that is, if we could point to a case of two transitions of any physical system from a given initial state to a given final state, for which the above sum were to have two different values, the possibility of constructing a " perpetual motion " machine would arise in that the configuration could be brought along the one route to the final state and then back along the other route to the initial state. The whole process then constitutes a " cycle." Now a cycle can be repeated any desired number of times and so gives us a machine which functions regularly, its effect being represented by the difference of the mechanical equivalents corresponding to the two individual transitions. By the energy principle this difference is nil, as can also be seen directly from (38) if we consider that for a cycle $E' = E$, and hence for every cyclic process the algebraic sum of the mechanical equivalents of all external actions must satisfy:

$$A + P + Q = 0 \quad . \quad . \quad . \quad (39)$$

This excludes the possibility of realizing a perpetual motion machine.

Since the choice of the physical systems to be considered is quite open, the energy principle (38) may be applied to a definite physical event in very different ways. For example, we may eliminate all external actions by including the body or bodies, to which the action is due, in the physical system. The external action in question is then disposed of and instead of it there appears a new term in the energy E of the system. In this way it is possible, by extending the system appropriately, to dispose of all external actions and to isolate the system so that its energy can be regarded as constant. It is not possible, of course, to take measurements if the configuration is *completely* isolated from its surroundings, for every measurement requires communication with the outside world.

§ 19. The quantity of heat Q taken up by a body may be of a mechanical or an electrical nature. According as the case may be we speak of *heat conduction* or *heat radiation.* But in each case the quantity Q refers only to the heat transmitted to the body and not, say, to the heat "contained" in the body. To be able to give a definite meaning to the latter concept general thermodynamics does not suffice; it becomes necessary to introduce a special hypothesis about the atomic constitution of bodies. All that can be measured directly, independently of any hypothesis, is the *transmission* of heat, not the thermal state in terms of energy. It is in agreement with this circumstance, too, that by equation (38) only energy *differences* can be measured; that is, the value of the energy E of a body always contains an indefinite additive constant.

In the first two parts of the present volume we shall consider only heat conduction, leaving heat radiation to be dealt with in the third part. Further we shall in general restrict our attention to considering bodies at rest. The energy E of a body then reduces to its so-called "internal" energy U which, like the pressure p, is to be regarded as a function which is determined by the chemical constitution, the temperature θ and the volume $V = Mv$ of the body, apart from an additive constant. If we also leave out of account external electromagnetic actions the equation of energy (38) reduces to the form

$$U' - U = A + Q \quad . \quad . \quad . \quad . \quad (40)$$

§ 20. Since Q denotes the mechanical equivalent of the heat transferred to the body, it is understood that Q is expressed in mechanical units (ergs, I, § 47). In thermal measurements, however, practical considerations lead us to use a special unit, the *calorie*. This is the quantity of heat which 1 grm. of water must take up from without in order that its temperature may rise from 14·5° C. to 15·5° C. All calorimetric measurements are expressible in terms of this unit.

The ratio of the quantity of heat Q taken up by a body to the resulting increase of temperature $\theta' - \theta = \Delta\theta$ is called the "mean heat-capacity" of the body between the temperatures θ and θ' :

$$\frac{Q}{\Delta\theta} = C_m$$

The heat capacity of 1 grm. of a substance is called its "specific heat."

$$c_m = \frac{C_m}{M} = \frac{Q}{M \, . \, \Delta\theta} = \frac{q}{\Delta\theta}$$

Accordingly the mean specific heat of water between 14·5° C. and 15·5° C. is equal to one calorie. If we make the temperature intervals infinitely small we obtain the so-called "true heat-capacity" of a body and the "true specific heat" of a substance, respectively, at the temperature θ :

$$\frac{Q}{d\theta} = C \text{ and } \frac{q}{d\theta} = c \quad . \quad . \quad . \quad . \quad (41)$$

which in general varies only slightly with the temperature.

To be rigorous the above definitions of heat-capacity and of specific heat require to be supplemented. For since the internal state of a body, besides depending on the temperature, also depends on a second variable, say the pressure, the change of state associated with an increase of temperature is not definite until we know how the second variable behaves in the process. In the case of solid and liquid bodies, it is true, the heat-capacity is almost independent of whether the heating is performed at constant or variable external pressure; for this reason we do not usually add a particular condition about the pressure in defining the heat capacity of such bodies. In the case of gases, however, the value of the heat capacity depends very decidedly on the external circumstances under which the heating process is carried out; hence, for them, the definition of heat-capacity must be supplemented by having these external circumstances specified, which can, of course, be controlled at will. The heat-capacity of a gas is taken simply to be that at constant atmospheric pressure, since this can be most conveniently measured.

§ 21. To enable calorimetric measurements to be used in applying the energy equation (40) it is necessary to know the factor which converts the unit of heat, the calorie, into the mechanical unit, the erg. This conversion factor, called the mechanical equivalent of heat, is a constant which depends only on the system of measurement used; its value may be found most directly by making a system pass from a definite initial state to a definite final state in one case by external mechanical means alone and in another case by means of external heat processes alone. For since $E' - E$ has the same value in both cases the mechanical equivalents of the external actions are equal in both cases, by (40), and the mechanical work A in the first case is equal to the heat Q transferred to the system in the second case.

Such measurements were first carried out by J. P. Joule, who caused a liquid (water, oil) to pass by two routes from a definite state of lower temperature to a definite state of higher temperature. This was done in the one case only by adding a certain quantity of heat, in the other only by performing a certain amount of mechanical work by means of the friction caused in the liquid by paddle-wheels which were made to turn by falling weights. In this process no importance attaches to the ideas we may have about the manner in which the heat is generated by friction; all that matters is that the final state of the liquid must be the same as that produced by the transfer of heat to the system. The measurements indicated that a calorie is equivalent to $4{\cdot}19.10^7$ ergs; consequently the mechanical equivalent of heat is:

$$a = 4{\cdot}19\,.\,10^7 \text{ ergs/cal.} \qquad (42)$$

This numerical value has subsequently been tested by numerous measurements. The fact that it always comes out as practically the same in all kinds of experiments with different substances, temperatures, friction apparatus and weights is a striking experimental confirmation of the law of conservation of energy (40).

§ 22. We shall now apply the first law of thermodynamics to a homogeneous body of given mass M whose state is defined by its temperature θ and its volume V. Here and everywhere in the sequel we shall use the word "homogeneous" simply in the sense of "physically homogeneous," that is, a homogeneous configuration is one whose smallest visible parts (in the macroscopic sense, cf. § 115 below) may be regarded as exactly of the same kind. It is not a question of the body being chemically homogeneous, that is, consisting of exactly similar moles throughout. For a partly dissociated vapour (§ 17) can very well be physically homogeneous. All that we wish to assume here is that the state of the homogeneous body in question is uniquely determined by the temperature and volume no matter whether or what sort of internal chemical transformations occur in the course of the changes of state under consideration. The pressure p and the internal energy U are then to be regarded as definite functions of θ and V.

Whereas the pressure p may be measured directly the energy equation (40) must be applied if we wish to determine the energy function U. We shall first consider the particular case of a gaseous body.

§ 23. If we allow a gas which is initially in thermal equilibrium and has an amount U of internal energy to flow out of one vessel into another, previously evacuated, a number of complicated mechanical and thermal changes will take place within the gas during this process. The issuing part of the gas will set itself into rapid motion and will afterwards become warmer owing to collision with the walls of the second vessel and the compression of the immediately following masses, while the part which remains in the vessel will become cool owing to expansion, and so forth. If we assume that the walls of both vessels are absolutely rigid and are perfect non-conductors of heat, then in equation (40) both $A = O$ and $Q = O$, and the energy of the gas remains constant. This energy is composed of many parts, namely of the kinetic energies and the internal energies of all the individual gas particles. If, however, we wait sufficiently long, until a completely steady state and thermal equilibrium have become established, the energy in the final state again consists only of internal energy, and it then follows from (40) that $U' = U$. But the variables θ and V, on which U depends, have passed from their original values to the values θ' and V', V' being greater than V. We may also find out by measuring the temperature and the volume before and after the process how the temperature θ of the gas varies as the volume V changes, while the internal energy U remains constant.

Joule carried out an experiment of this kind and found that for gases θ' is nearly equal to θ. He placed the two vessels, one of which was initially filled with air at high pressure and the other evacuated, in a common water-bath at the same temperature. On carrying out the above process of allowing the gas to stream into the vacuum and after waiting for the state of equilibrium to be attained, he found that the change of temperature in the water-bath was inappreciably small. From this it follows that even in the case of walls that are perfect non-conductors of heat the final temperature of the gas is equal to the initial temperature; for otherwise the change of temperature would have been communicated to the water in the above experiment.

Thus when the internal energy of a gas remains constant while its volume is changed, the temperature also remains practically constant; or, in other words, the internal energy of a gas is determined almost entirely by the temperature alone and is independent of the volume.

§ 24. To make this conclusion appear quite convincing still more accurate measurements are necessary. For in the experiment by Joule just described the heat-capacity of the gas is so small compared with that of the walls of the vessel and the water-bath that it would have required a very considerable change of temperature in the gas to produce a measurable change of temperature in the water. An essential modification of the method was devised by W. Thomson (later Lord Kelvin) and carried out by him in conjunction with Joule; this allowed refined measurements to be made which gave more trustworthy results. It consists in artificially retarding the outflow of gas so that it passes directly into its second state of thermal equilibrium and the temperature θ' is then directly measured in the gas. It does not in this case stream out tumultuously as a limited mass of gas into a vacuum; rather the gas is led in an unlimited steady stream from the region of higher pressure into that of lower pressure by being forced through a cylindrical tube of beech-wood which is blocked at one point by a porous plug of cotton wool or teased silk (shown shaded in Fig. 2).

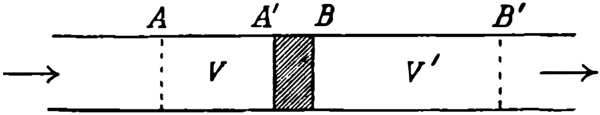

FIG. 2.

This enables us to draw an inference about the internal energy of a gas. For this purpose we apply the energy equation (40) to the system AB when the stream has become steady; the system AB consists of a mass of gas which is on the left side of the porous plug (we reckon it from an arbitrary cross-section A) and the plug together with the gases contained in it. Let the volume of the gas between A and A' be V. We shall choose as our final state that which exists when the gas particles which were originally in A have reached the boundary A' of the plug. At this moment those gas particles which were initially at the cross-section B have now arrived at B'. The masses of gas AA' and BB' are then equal, whereas their volumes V and V' will of course be different. Let us next calculate the mechanical equivalent $A+Q$ of the external forces acting on the configuration in question. The transferred heat Q is nil; for the wood of which the tube is composed is practically a perfect non-conductor, and at A and B' there is no conduction of heat because the temperatures θ and θ' in the gas are constant. There then only remains the mechanical work which is performed by the external forces of pressure acting on the slowly moving system. The force acting on its left side is equal to the pressure multiplied by the cross-section of the tube; the displacement of the system AA' is equal to the volume V divided by the cross-section of the tube. Hence the work done, namely the product of the force and the displacement, is equal to pV. On the right side of the plug the work done is correspondingly equal to $-p'V'$, because here the displacement is in the sense opposed to the external force, which acts from right to left. So the total external work is $A=pV-p'V'$. Now the difference of energies of the system in question in the initial and in the final state clearly reduces to the difference of the internal energies U and U' of the equal masses of gas AB and $A'B'$. For the plug and the gas contained in it are in the same state at the end as at the beginning. However complicated the events that occur in the plug may be, they do not come into consideration for the energy equation so long as the process is steady. All in all we find then that if we apply the energy equation (40) to the steady process in question we have:

$$U' - U = pV - p'V' \quad . \quad . \quad . \quad . \qquad (43)$$

This is the general theory of Joule and Thomson's porous plug experiment.

As for the results obtained by actual measurement it was found that in the case of air in the steady state there was a very small change of temperature $\theta - \theta'$ in the gas on the two sides of the plug; in the case of hydrogen it was still smaller, being hardly measurable. From this it follows by (9) that the right-hand side of equation (43) and hence also the left-hand side, $U' - U$, almost vanishes. That is, the internal energy of the gas has remained, like the temperature, almost unchanged in spite of its greatly changed volume, and the inference already drawn at the end of § 23 that the internal energy of a gas at a definite temperature is almost independent of its volume is confirmed, namely that:

$$\left(\frac{\partial U}{\partial V}\right)_\theta = 0 \quad . \qquad (44)$$

§ 25. Those processes which, as it is usually expressed, occur infinitely slowly and therefore consist of states of equilibrium alone are of particular importance for the theory. Taken literally this mode of expression is not precise, for the nature of a process necessarily involves changes, that is, it assumes disturbances of the state of equilibrium. But if we are concerned, not with the time but only with the final result of the changes we may assume these disturbances to be as small as we please compared with those quantities which are characteristic of the state of the system in question. For example, we can compress a gas as slowly as we wish to any fraction of its initial volume by making the external pressure at every moment very slightly smaller than the pressure of the gas, and in calculating the external work only a very small error is incurred if we use the pressure of the gas instead of the external pressure. In passing to the limit this error disappears altogether and the result becomes rigorously accurate. For the error in a definite result always has a definite value, and if this error is smaller than any arbitrarily small quantity, it is of necessity equal to zero.

What has just been said applies equally well to a compression at constant pressure as to one in which the pressure is varying. In the latter case the exactly appropriate value must be given to the external pressure at every moment. This can be achieved by means of special regulating devices which do not involve the performance of work.

The position with heat that has been taken up or given out is just the same as with the external work. If we are concerned with the value of the quantity of heat which a body has received from or given to its surroundings it is sufficient to assume the temperature of the heat-container used to be greater or smaller by an arbitrarily small value than the temperature of the body, according as the heat is taken up or given out. This slight excess simply determines the direction of the process but its value does not come into question compared with the *whole* change produced by the process. For this reason just as we spoke of the compression of a gas by means of an external pressure equal to that of the gas so also we speak of the transference of heat from one body to another at the same temperature; and doing this means only that we anticipate the result which is obtained in passing to the limit by making the finite small difference of temperature of the two bodies become vanishingly small.

This also applies not only to isothermal processes but also to those in which the temperature varies. In the case of the latter it is not sufficient to have a single heat-reservoir at constant temperature but rather we must have a sufficiently great number of appropriate heat-reservoirs at different temperatures and must at each moment use just that reservoir whose temperature is as nearly as possible equal to that of the body under consideration.

The great theoretical importance of the point of view underlying this method of treatment is that every "infinitely slow" process can be imagined to be carried out in the reverse direction. For if a process consists, except for extremely small changes, of nothing but states of equilibrium, then clearly an equally small change appropriately applied will always suffice to make the process occur in the reverse direction, and the magnitude of this very small change can, as above, be made vanishingly small by passing to the limit.

§ 26. We now proceed to apply the first law of thermodynamics to a process of this kind which consists only of states of equilibrium and is therefore reversible. It may be pictured graphically in a simple way by plotting the series of equilibrium states successively passed through by the body as a curve in the plane of a coordinate system whose axes represent the values of the independent variables. We shall here again choose as our independent variables the volume V (abscissae) and the pressure p (ordinates). Corresponding to every point in the co-ordinate plane there is then a definite state of the homogeneous body in question and every curve denotes a definite continuous and reversible change of state. A reversible process, for example, which brings the body from a state 1 to a state 2 is indicated by a curve α which passes from the point 1 to the point 2 (Fig. 3). By equation (40) the increase of energy of the body is:

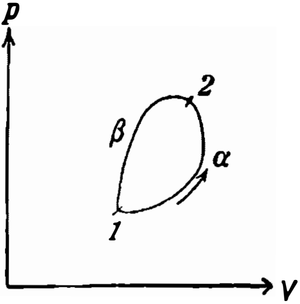

FIG. 3.

$$U_2 - U_1 = A + Q \quad . \quad . \quad . \quad . \quad (45)$$

where A denotes the work done by the external pressures and Q the heat transferred to the system from without.

§ 27. The value of A can be calculated directly. For A is the algebraic sum of the elementary portions of work which are performed by the external pressure during the successive infinitely small changes of the body, corresponding to the individual elements of arc of the curve α. Now since the external pressure at any moment is to be set equal to the pressure p of the body—as the process is assumed to be reversible—the external work done in an infinitely small change of state is, by II (278), in general equal to $-p\,.\,dV$ and is independent of the shape of the surface of the body. Accordingly the external work done during the course of the whole process is :

$$A = -\int_1^2 p\,.\,dV\,. \qquad . \qquad (46)$$

where the integration is to be taken along the curve α from the point 1 to the point 2. If p is positive, as in the case of gases, and $V_2 > V_1$, as in Fig. 3, then A is negative; that is, no external work is done on the gas but work is done by the gas, say, by raising a weight which is pressing down on the gas.

To be able to carry out the integration it is necessary to know how the pressure p depends on the volume V, that is, we must know the shape of the curve α. So long as only the points 1 and 2 are known and the connecting curve is not given, the integral has no definite value. Thus if the transition from 1 to 2 occurs along another curve β the result of the integral will be quite different. Hence the differential pdV is, we may say, an "incomplete differential." Regarded mathematically, this circumstance is due to the fact that besides depending on V the quantity p also depends on another variable, the temperature θ, which will change in a certain way in passing along the path of integration α. So long as α is not known nothing can be said about the dependence of θ on the integration variable V; and so the integration cannot be performed.

The external work A has a very simple graphical meaning in Fig. 3. By (46) it is clearly equal to the negative value of the area of the figure enclosed by the curve α, the V-axis and the ordinates through the points 1 and 2. From this, too, we see that the value of A is essentially conditioned by the course of the curve α. It is only for infinitely small changes of state, that is, when the points 1 and 2 are infinitely close to each other, or when α contracts to a curve element, that A is determined by the initial and final point of the curve alone.

§ 28. From the value (46) for A and the energy equation (45) the heat transferred to the body comes out as :

$$Q = U_2 - U_1 + \int_1^2 pdV \quad . \qquad . \quad (47)$$

From this we see that the value of Q as well as that of A is conditioned not by the points 1 and 2 alone but also by the shape of the curves α and β that connect them. In addition, to be able to calculate Q, we require to know the energy U of the body in the states 1 and 2.

The quantity Q can be calculated independently of the energy U in the case where the body is finally again brought to its initial state 1, that is, when it performs a cycle. This can happen, for example, when it is first brought to the state 2 along the path α and then back to the state 1 along the path β. For then, as has already been shown in § 18 :

$$Q = -A = \int_1^1 pdV \quad . \quad . \quad . \quad . \quad (48)$$

where the integral is to be taken over the closed curve 1 α 2 β 1. A at the same time represents the area of the surface enclosed by this composite curve; it is positive when the cycle takes place in the direction indicated by the arrow (Fig. 3).

Such a cycle, when performed any number of times in the appropriate direction, represents the type of a machine working periodically, which continually converts heat into mechanical energy.

§ 29. In this paragraph we shall consider more closely the special case in which the curve α characteristic of the change of state contracts into a curve element and so brings the points 1 and 2 infinitely close to each other. Equation (47) then becomes: $dQ + dW$

$$Q = dU + pdV \quad . \quad . \quad . \quad . \quad . \qquad (49)$$

Referred to unit mass of the body this equation runs:

$$q = du + pdv \quad . \quad . \quad . \quad . \quad . \qquad (50)$$

if the quotients of Q, U and V by the mass M are denoted by the corresponding small letters. An important consideration for the following calculations is to know which of these quantities are used as independent variables. It is usual to take the temperature θ for one and either the volume v or the pressure p for the other. We shall choose the independent variable according to requirements and, to avoid confusion, we shall specially note the sense of the differentiation.

We shall now apply equation (50) to the most important properties of a homogeneous body.

§ 30. By (41) and (50) the specific heat of the body is:

$$c = \frac{q}{d\theta} = \frac{du}{d\theta} + p\frac{dv}{d\theta} \quad . \quad . \quad . \quad . \qquad (51)$$

As has already been emphasized in § 20 this quantity has a definite value only when the manner of heating is specified. Actually, the differential quotients in (51) acquire a meaning only when an equation of condition between the two independent variables, say θ and v, is given. The most important cases are those in which either the volume v or the pressure p is kept constant during the heating process.

When heat is added at constant volume we have $dv = 0$, and by (51) we get for the specific heat at constant volume:

$$c_v = \left(\frac{\partial u}{\partial \theta}\right)_v . \qquad (52)$$

When heat is added at constant pressure $dp = 0$, and by (51), the specific heat at constant pressure is:

$$c_p = \left(\frac{\partial u}{\partial \theta}\right)_p + p\left(\frac{\partial v}{\partial \theta}\right)_p \qquad (53)$$

or, since:

$$\left(\frac{\partial u}{\partial \theta}\right)_p = \left(\frac{\partial u}{\partial \theta}\right)_v + \left(\frac{\partial u}{\partial v}\right)_\theta \cdot \left(\frac{\partial v}{\partial \theta}\right)_p$$

we have, taking into account (52):

$$c_p = c_v + \left(\left(\frac{\partial u}{\partial v}\right)_\theta + p\right)\left(\frac{\partial v}{\partial \theta}\right)_p \quad . \quad . \quad . \quad (54)$$

§ 31. Let us apply the last equation to a gas. For this we have by (44):

$$\left(\frac{\partial u}{\partial v}\right)_\theta = 0$$

and by (34):

$$v = \frac{2{\cdot}27 \, . \, 10^{10}}{mp}(1 + \alpha\theta)$$

Consequently we have by (54), bearing in mind (6):

$$mc_p - mc_v = \frac{2{\cdot}27 \, . \, 10^{10}}{273{\cdot}2} = 8{\cdot}31 \, . \, 10^7 = R \quad . \quad . \quad (55)$$

That is, the value of the difference of the molar heat at constant pressure and the molar heat at constant volume is almost the same value for all gases, namely R.

There are difficulties in subjecting this formula to a direct experimental test because in the case of a gas only the specific heat c_p at constant pressure can be conveniently measured, but not the specific heat at constant volume. For a quantity of gas contained in a closed vessel of constant volume has a far too small heat capacity compared with external bodies, in particular the walls of the vessel, to be able to produce thermal effects measurable with ordinary apparatus (cf. § 23 above). But nevertheless the equation (55) admits of an important practical consequence in itself. For since, by (52), c_v like u depends only on the temperature and not on the volume, the same follows by (55) for c_p.

This conclusion was first verified by the measurements of Regnault and was by no means obvious at the outset. On the contrary, in the older theory of heat due to Carnot, which regarded heat as an indestructible substance, it was inferred from the fact that a gas is heated by compression that the heat capacity of a gas is considerably diminished by reducing its volume, inasmuch as during the compression the heat is as it were pressed out of the gas in much the same way ~~as water is squeezed out of a wet sponge~~. Regnault's results prove that this view is untenable. Moreover Regnault found that c_p is constant over a fairly wide range of temperature. By (55) c_v is then also nearly constant over the same range of temperature, and by (52) the energy of the gas is :

$$u = c_v \, . \, \theta + \text{const.} \quad . \quad . \quad . \quad . \qquad (56)$$

The additive constant of integration is essentially indefinite (§ 19).

If the molar heat is not measured in mechanical units but in calories, the quantity R in (55) must of course be divided by the mechanical equivalent of heat a given in (42); and we have as the difference of the molar heats at constant pressure and constant volume :

$$\frac{R}{a} = \frac{8{\cdot}31 \, . \, 10^7}{4{\cdot}19 \, . \, 10^7} = 1{\cdot}983 \quad . \quad . \quad . \qquad (57)$$

According to the measurements obtained for all monatomic gases the molar heat is almost equal to 5; for diatomic gases it is nearly equal to 7, for polyatomic gases it is still greater. From this we obtain by (57) for the molar heat at constant volume the corresponding values of approximately 3, 5 and more. And so we get for the ratio of the two molar heats :

$$\kappa = \frac{c_p}{c_v} = \frac{5}{3}, \frac{7}{5} \; . \; . \; . \rightarrow 1 \; . \qquad (58)$$

As the number of atoms in the mole increases κ decreases without limit towards 1. A reason for this regular behaviour is given only by modern atomic theory (§ 144).

§ 32. Now how is the heating of a gas by compression to be explained on the theory that has been developed? To answer this question we need only apply the equation

(50) of the first law to a process in which the gas is compressed without heat being allowed to pass through the walls of the vessel, and which is therefore called "adiabatic." The condition $q = 0$ which is characteristic of adiabatic processes gives, by (50):

$$du + pdv = 0$$

and by (56) and (34):

$$c_v d\theta + \frac{2{\cdot}27 \,.\, 10^{10}}{mv}(1 + \alpha\theta)dv = 0$$

This differential equation may be interpreted term by term, if we first divide by $(1 + \alpha\theta)$. We then get:

$$\frac{c_v}{\alpha}\log(1 + \alpha\theta) + \frac{2{\cdot}27 \,.\, 10^{10}}{m}\log v = \text{const.}$$

or by (6) and (55):

$$mc_v \log(1 + \alpha\theta) + R\log v = \text{const.} \quad . \quad . \quad (59)$$

The values of the constants of integration are given by the initial state. By using the relation (55) and introducing the ratio κ of the specific heats (58) we may also write this in the form:

$$\log(1 + \alpha\theta) + (\kappa - 1)\log v = \text{const.} \quad . \quad . \quad (60)$$

and in this way we obtain the law of the increase of temperature with decrease of volume, which is completely determined by the numerical value of κ.

If we wish to know the adiabatic relation between the volume and the pressure, we must eliminate θ from (60) by means of the equation of state (34); for this purpose we conveniently write (34) in the form:

$$\log p + \log v - \log(1 + \alpha\theta) = \text{const.}$$

By adding the last two equations we then get:

$$\log p + \kappa\log v = \text{const.} \quad \text{or} \quad pv^{\kappa} = \text{const.} \quad . \quad . \quad (61)$$

as the law for the adiabatic compression of a gas. A comparison with the law of isothermal compression, $pv = \text{const.}$, shows that in adiabatic compression the pressure increases more rapidly as the volume decreases than in the case of isothermal compression, as is natural.

§ 33. Since by (61) adiabatic processes may be used to measure κ they furnish us with an important means of testing the theory since we can compare this value with the numerical values (58) calculated from the mechanical equivalent of heat.

For example, we can use the measurement of the velocity of sound in a gas to calculate κ. By II (293) this velocity is:

$$a = \sqrt{\frac{\kappa p}{k}}$$

where k denotes the density of the gas and is also equal to $\frac{1}{v}$. From this it follows that:

$$\kappa = \frac{ka^2}{p}$$

If in this formula we substitute for air at 0° C. and at one atmosphere pressure:

$$a = 33200 \text{ cms./sec.}$$
$$p = 1013000 \text{ grms./cm. sec.}^2$$

and, by II (284):

$$k = 0{\cdot}001293 \text{ grms./cm.}^3$$

we get $\kappa = 1{\cdot}40$ which agrees with the numerical value $\frac{7}{5}$ in (58) for a diatomic gas.

Of course we may conversely also use the value of κ calculated from the velocity of sound to calculate c_v in calories and then, by applying (55) to calculate the mechanical equivalent of heat. This method of evaluating the mechanical equivalent of heat was originally used by Robert Mayer in 1842. It is true that we must have for this purpose the relation (44) which expresses that the energy of the air is independent of its volume or, in other words, that the difference of c_p and c_v is conditioned only by the external work, as otherwise the general relation

(54) would have to be assumed—an assumption which could be regarded as directly proved only after the experiments of Joule and Thomson described in § 24 had been carried out.

§ 34. Leaving the reversible changes of state of a homogeneous body we next turn to those processes which are connected with changes of the aggregate state or chemical transformations. In each case we can again apply equation (47) to the process. In this equation Q then denotes the " heat of transformation " or " heat tone " (*Wärmetönung*) and is positive if the heat is transferred from without. In this process we always assume the final temperature θ_2 equal to the initial temperature θ_1. In changes of the aggregate state Q occurs with its appropriate sign as heat of vaporisation, heat of condensation, heat of fusion or heat of solidification; in chemical processes it occurs as heat of reaction, heat of combination, heat of solution, heat of dissociation and so forth. We see that the value of Q does not in general depend only on the initial and final states of the configuration in question but also on the path followed between these states and, in particular, on the external work. For processes which occur at constant volume as, for example, combustion in a hermetically sealed vessel, a so-called calorimetric bomb, we have $Q = U_2 - U_1$, that is, simply equal to the difference of the energies. On the other hand, for isobaric processes—such as most chemical processes are, as they occur at ordinary atmospheric pressure—we have:

$$Q = U_2 - U_1 + p(V_2 - V_1) \quad . \quad . \qquad (62)$$

or, referred to unit mass:

$$q = u_2 - u_1 + p(v_2 - v_1) \,. \qquad (63)$$

If we unite these equations in the form:

$$Q = (U + pV)_2 - (U + pV)_1$$

we see that in the case of isobaric processes, too, the heat of transformation depends only on the initial and the final states. But it is not represented as in isochoric processes by the difference of the energy U but by the difference of the function:

$$W = U + pV \quad . \quad . \quad . \quad . \quad (64)$$

which Gibbs calls the "heat function at constant pressure," while Mollier calls it the "enthalpy." For unit mass it is:

$$w = u + pv \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

In many cases, particularly in vigorous chemical reactions, but also in changes of the aggregate state in which no gases participate, the amount of the external work is so small compared with the heat of transformation Q that we can exchange the heat function at constant pressure with the energy without incurring an appreciable error. If the configuration contains gaseous parts in its initial or its final state, then, in calculating the external work, it is as a rule sufficient to consider these parts alone; that is, the volume change of the solid and liquid bodies may be neglected. If n_1 and n_2 are the numbers of gaseous moles in the initial and final state, respectively, we obtain, by (62) and (35), for an isobaric process, using mechanical units:

$$Q = U_2 - U_1 + 2{\cdot}27 \,.\, 10^{10} (n_2 - n_1) \,.\, (1 + \alpha\theta) \quad . \quad (66)$$

Thus the amount of the external work done depends only on the change in the number of gaseous moles and the temperature, but not on the pressure.

The fact that the heat function W at constant volume plays the same part in isobaric processes that the energy U plays in isochoric processes also manifests itself in the case of the specific heats. For, corresponding to the equation (52) for c_v we have the equation:

$$c_p = \left(\frac{\partial w}{\partial \theta}\right)_p \quad . \quad . \quad (67)$$

which, on account of (65), is identical with (53).

§ 35. Since the heat of transformation Q refers to a definite temperature θ the value of Q will in general depend on θ. There is a simple relation for this dependence, which is obtained by differentiating Q with respect to θ.

For in the case of isochoric transformations $Q = U_2 - U_1$, and:

$$\left(\frac{\partial Q}{\partial \theta}\right)_V = \left(\frac{\partial U_2}{\partial \theta}\right)_V - \left(\frac{\partial U_1}{\partial \theta}\right)_V = (C_V)_2 - (C_V)_1 \,. \qquad (68)$$

On the other hand, for isobaric transformations we have $Q = W_2 - W_1$, and by (67):

$$\left(\frac{\partial Q}{\partial \theta}\right)_p = \left(\frac{\partial W_2}{\partial \theta}\right)_p - \left(\frac{\partial W_1}{\partial \theta}\right)_p = (C_p)_2 - (C_p)_1 \,. \qquad (69)$$

where C_V and C_p denote the heat capacities of the system at constant volume and constant pressure, and the indices 1 and 2 refer to the state of the configuration before and after the transformation.

Thus we find the influence of temperature on the isobaric heat of combustion of hydrogen in forming liquid water by subtracting the isobaric heat capacity of an explosive mixture of oxygen and hydrogen (state 1), consisting of one mole of hydrogen and half a mole of oxygen, from the heat capacity of one mole of liquid water (state 2). Since, by § 31, the molar heat of hydrogen and oxygen is 7 and the specific heat of water is 1, while its molar weight is 18, we have:

$$(C_p)_1 = 7 + \frac{1}{2}\cdot 7 = 10{\cdot}5$$

$$(C_p)_2 = 18\,.\,1 = 18.$$

Hence, by (69):

$$\left(\frac{\partial Q}{\partial \theta}\right)_p \doteq 18 - 10{\cdot}5 = 7{\cdot}5.$$

Now in the present case Q is negative because the heat of reaction is given to the surroundings. Consequently the amount of the heat of combustion of a mole of hydrogen decreases by 7·5 calories per degree as the temperature increases.

CHAPTER III

SECOND LAW OF THERMODYNAMICS

§ 36. The content of the second law of thermodynamics is sharply distinguished from that of the first law because it concerns a question which is not touched on by the latter at all, namely the question of the direction in which a thermal process occurs in nature. For not every change which is compatible with the principle of conservation of energy satisfies the further condition imposed by the second law on the processes that actually occur in nature. If, for example, an exchange of heat occurs by conduction between two bodies at different temperatures, the first law requires only that the amount of heat given out by the one body should equal the amount of heat taken up by the other body. Whether the heat conduction occurs in the one or the other direction cannot be decided on the strength of the first law. Indeed, the concept of temperature is in itself foreign to the energy principle, as can be seen from the fact that this principle does not lead to an exact definition of temperature.

As for the direction in which processes occur in nature and the way in which this question is answered by the second law there is an essential difference between mechanical and electrodynamic events on the one hand and thermo-chemical events on the other hand—a difference to which we have already alluded in § 2. For whereas the former can always also occur in the exactly opposite direction—a heavy body can rise just as well as it can fall, a spherical electrodynamic wave can propagate itself just as well inwards as outwards—according to the second law no thermal event can be directly reversed.

The problem of formulating the second law correctly has occupied physicists for decades. A long time passed before it was recognized that the content of the second law is not exhausted if—as was done occasionally even by Clausius and later with renewed emphasis by Ostwald—every process in nature is resolved into a series of energy transformations and the direction of each individual transformation is enquired into. It is true that in each individual case we can name the different kinds of energy that are transformed into one another—this follows from the first law—but there always remains a certain arbitrariness as to how the individual transformations are allocated to one another, and this arbitrariness cannot be removed by a general convention.

Even nowadays the nature of the second law is sometimes sought in the tendency of natural phenomena to "degrade" energy on the ground that, for example, mechanical energy can be completely transformed into heat but heat can be transformed only incompletely into mechanical energy, in the sense that if a quantity of heat is transformed into mechanical energy then another transformation, such as a thermal transition from a higher to a lower temperature which serves as a compensation process, must always occur simultaneously.

That this formulation, which is useful in special cases, by no means gets to the root of the matter can be seen from the following simple illustration. If a gas is allowed to expand, doing work in the process, and if at the same time the temperature of the gas is kept constant by the transference of heat from a reservoir at a higher temperature, we may say that the heat transferred by the reservoir has been *completely* transformed into work. For while the gas has retained its temperature it has also retained its internal energy unchanged (§ 24), and other transformations of energy are not occurring. No fact of any kind can be objected to in this assertion. But in the case of the second law we are concerned with particular facts that can be ascertained by measurement. That is also why the second law cannot be deduced *a priori*. We can speak of proving it only in so far as its total content may be deduced from a single simple fact of experience of convincing certainty.

§ 37. In connexion with what has just been said we shall now base the general proof of the second law on the following empirical law: "it is impossible to construct a machine which functions with a regular period and which does nothing but raise a weight and cause a corresponding cooling of a heat reservoir."

Such a machine could be used simultaneously as a motor and as a cooling machine without any other expenditure of energy or materials. It would at any rate be the most advantageous in the world. It would not be equal to the perpetual motion machine, for it by no means produces work from nothing, but from the heat which it abstracts from the reservoir. That is also the reason why it does not, like the perpetual motion machine, conflict with the first law. But it would nevertheless possess the most essential advantage of the perpetual motion machine for mankind, that of supplying work without expenditure. For the heat contained in the soil, in the atmosphere and in the ocean is always available, just like the oxygen of the air, in inexhaustible quantities for direct use by anyone. This circumstance also accounts for our beginning with the above empirical law. For as we shall deduce the second law from it we secure for ourselves, in the event of our ever discovering any deviation of a natural phenomenon from the second law, the prospect of immediately being able to apply it practically in a very important way. For as soon as any phenomenon is found that contradicts a single inference from the second law, the contradiction would be due to an inaccuracy in the very first assumption on which it is based and it would be possible, by following the above reasoning backwards step by step, to use the phenomenon to construct the machine above mentioned. For the sake of brevity we shall in the sequel follow a suggestion of Ostwald and call it a "perpetual motion machine of the second kind," since it bears the same relation to the second law that the perpetual motion machine of the first kind bears to the first law.

§ 38. If we compare the two kinds of perpetual motion machine we at once observe a fundamental difference: the law forbidding the perpetual motion machine of the first kind also applies conversely, that is, work can neither be produced absolutely nor annihilated absolutely, whereas the law which forbids the perpetual motion machine of the second kind does not apply conversely; that is, it is certainly possible to construct a machine which does nothing more than lower a weight while a heat reservoir is correspondingly warmed. As an illustration of this kind of machine we have that used by Joule to measure the mechanical equivalent of heat; it is set into motion by means of a falling weight which causes rotating paddle-wheels to warm a liquid by friction. For if the weight reaches the floor with vanishingly small velocity no change has taken place in nature except that the liquid—which is here to be regarded as a heat reservoir—has been warmed. In fact it is clear that every frictional process represents a reversed perpetual motion machine of the second kind, so that our empirical law stated above may also be formulated as follows: there is no possible way of completely reversing a process in which heat is generated by friction. The word "completely" is used here to express that the initial state of the frictional process has everywhere been exactly restored. To take a definite example, if after a Joule's friction experiment had been carried out it were possible by some process to bring the fallen weight back to its original height and to cool the liquid correspondingly without any other changes remaining this would obviously be a perpetual motion machine of the second kind. For it does nothing beyond raising a weight and correspondingly cooling a heat reservoir.

For the sake of brevity we shall call a process which can in no way whatsoever be completely reversed "irreversible" and all other processes "reversible." For a process to be reversible, then, it is not sufficient to restore the bodies that participate in the process to their initial state—this is always possible in principle—but it is required that it should in some way be possible to restore the initial condition of the process everywhere in nature, no matter what technical devices and mechanical, thermal, chemical and electrical apparatus are used. All that is essential is that any material and apparatus used should at the end be again in exactly the same state as in the beginning when they were taken for use.

§ 39. Any process that occurs in nature is either reversible or irreversible. We have as examples of reversible processes all purely mechanical and electrodynamic processes. For if they occur in the reverse direction the initial state is completely restored. As an example of an irreversible process we have had the generation of heat by friction; other examples will be given in the sequel.

The significance of the second law consists in the fact that it furnishes us with a necessary and sufficient criterion as to whether a definite process that occurs in nature is reversible or irreversible. Since the decision on this question depends only on whether the process can be completely reversed or not, we are concerned only with the constitution of the initial state and the final state of the process but not on its intermediate course. For it is merely a question as to whether, starting from the final state, we can or cannot again arrive at the initial state without anything being changed. Hence the second law furnishes for any process whatsoever in nature a relationship between those quantities which refer to the initial state and those which refer to the final state. In the case of irreversible processes the final state is distinguished by a certain property from the initial state, whereas in the case of reversible processes these two states are in a certain sense of equal value. We shall express this briefly by saying that in the case of an irreversible process the final state has a greater "thermodynamic probability" or a greater "thermodynamic weight" (we say "thermodynamic" to distinguish it from "mathematical" probability or mechanical weight, respectively) than the initial state. These words are to convey no more than what has been said above. We may then formulate the content of the second law by saying that it gives us a measure of the magnitude of the thermodynamic probability or the thermodynamic weight of a physical configuration in a given state. Our next task is to find this measure.

§ 40. To solve this problem we shall adopt the following course. Let us imagine an arbitrary system of bodies and let us consider any two different and exactly defined states of the system, which we shall denote by Z and Z'.

The question is whether and under what conditions a process in nature is possible such that it transfers the system of bodies in some way from the state Z to the state Z' or conversely, without anything being left changed outside the system. We can make the last proviso superfluous by including all the bodies in the world in the system under consideration. In other words, our object is to specify to which of the two states Z and Z' the greater thermodynamic probability is to be assigned. There are clearly three different possibilities. A transition may be possible both from the state Z to the state Z' and also conversely from Z' to Z; this process is then reversible every time and, indeed, in all its parts, and so the probabilities are equally great for both states. Or a transition may be possible from Z to Z' but not reversely from Z' to Z; the process in question is then irreversible and the probability of Z' is greater than that of Z. Or, lastly, the opposite case may occur, namely if an irreversible process from Z' to Z is possible of execution, so that Z has a greater probability than Z'.

If the definition of the two states Z and Z' is quite arbitrary at the outset, they must nevertheless fulfil the condition that the transition from one state to the other involves the loss neither of matter nor of energy. For otherwise the process in question would be impossible from the very start. The system of bodies must therefore have the same chemical constituents and the same energy in both states. Otherwise, however, Z and Z' may be selected arbitrarily.

§ 41. We start from the simplest case that the states Z and Z' are distinguished from each other only by the behaviour of a single homogeneous body of the kind considered above in § 22. Let this body have the volume V and the temperature θ in the state Z, the temperature being measured by any thermometer, for example, a mercury thermometer or any gas thermometer; and in the state Z' let it have the volume V' and the temperature θ'. The volume and the temperature also determine the energies of the body, U and U', respectively. Since U and U' are in general different from each other and since on the other hand we must ensure that the transition from Z to Z' satisfies the energy principle, we imagine an invariable weight G included in the configuration in question, the centre of gravity of this weight being at a height h in the state Z and at a height h' in the state Z', so that:

$$G.(h - h') = U' - U \quad . \tag{70}$$

From the standpoint of the energy principle a transition of the system from one state to the other is possible without anything remaining changed outside the system.

We now start from the state Z and endeavour to reach the state Z'. To do this we first subject the body in question to a reversible adiabatic change, as was done in § 32 with a gas. We then have $Q = 0$ and by (49):

$$dU + pdV = 0 \quad . \tag{71}$$

Also:

$$dU = \left(\frac{\partial U}{\partial \theta}\right)_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV$$

Thus we get:

$$\left(\frac{\partial U}{\partial \theta}\right)_V d\theta + \left\{\left(\frac{\partial U}{\partial V}\right)_\theta + p\right\} dV = 0$$

The expression on the left-hand side is not a complete differential, as we saw in § 27. But there is always an "integrating factor" N, that is, a function of the two independent variables θ and V which when divided into the expression makes it a complete differential, so that we may always write:

$$\frac{dU + pdV}{N} = dS \quad . \qquad (72)$$

where S is now a finite function of the two independent variables θ and V. We may thus regard S, just like the energy U, as a definite property of the state of the body. We shall follow Clausius and call it the "entropy" of the body in the state defined by θ and V.

But the definition of the entropy given by (72) is not yet unique. For there is not only one, but, indeed, an infinite number of quantities N, which when divided into the expression (71) make it a complete differential. This is easily seen by writing $N . f(S)$ instead of N, where f denotes any arbitrary function of a single variable. Corresponding to every expression for f there is then a different complete differential (72) and hence a different definition for the entropy.

Hence there is in the quantity N one factor, dependent only on S, which can be selected arbitrarily; and to complete the definition of entropy it is necessary to fix this factor. For the present, however, we shall leave our decision on this question open and shall calculate for the present with any arbitrarily chosen N, which we take as positive:

$$N > 0 \quad . \; . \; . \; . \; . \; . \; . \qquad (73)$$

The following theorems hold independently of the arbitrariness still left in the definition of entropy.

Now that S has been determined by (72) we may integrate the differential equation (71) and we obtain:

$$S = \text{const.} \quad . \; . \; . \; . \; . \; . \qquad (74)$$

a definite relation between θ and V which holds for the process described, or a relation between U and V, the so-called reversible adiabatic relation.

§ 42. To pass from the state Z to the state Z' let us now make V transform into V', U transforming into U' during the process, by (74). At the same time a certain amount of mechanical work is performed by or on the system; let it correspond to the transference of the weight G from the height h to the height h^*. We have, by the energy principle:

$$G\,.\,(h^* - h) = U - U^*$$

or, by (70):

$$G\,.\,(h^* - h') = U' - U^* \qquad . \qquad (75)$$

Three cases are then possible:

1. $U^* = U'$. The body then satisfies the conditions of the state Z', and since the weight G is then also at the height $h^* = h'$ determined by (75), the state Z' is completely attained; the desired transition is then realizable, the process being reversible. Thus in this case the states Z and Z' have the same probability.

2. $U^* < U'$. The transferred energy of the body, U^*, is then less than in the state Z'. In this case the state Z' may be attained by heating the body by friction, the volume V' being kept constant; this is done by allowing the weight G which, by (75), is situated at the height $h^* > h'$, to sink to the level h'. The state Z' is then completely realized but now, according to § 39, by an irreversible process, that is, the state Z' possesses a greater probability than the state Z.

3. $U^* > U'$. Then $h^* < h'$ and the transition to the state Z' is impossible as it would represent a perpetual motion machine of the second kind (§ 38). Hence in this case the state Z has a greater probability than the state Z'.

Let us next enquire into the behaviour of the entropy of the body in question in the three different cases. By the definition of entropy (72) and by (73) the entropy changes in the same sense as the energy, if the volume remains constant ($dV = 0$). Now when the volume V' and the energy U^* are attained the entropy has retained its original value S by (74), the difference of S and S', that is, the difference of the entropies of the states (V', U^*) and (V', U') has the same sign as the difference of U^* and U'. Thus in the first case $S = S'$; in the second $S < S'$; in the third $S > S'$.

From this it also follows conversely that according as the entropy S' of the body in the state Z' is just as great, greater than or less than the entropy S of the body in the state Z, the state Z' has a probability which is just as great as, greater than or smaller than that of the state Z.

§ 43. The last deduction leads us directly to a theorem of far-reaching importance. If any arbitrary physical configuration has passed by means of some reversible physical or chemical process from a state Z to another state Z', which differs from the state Z only by the circumstance that a single body of the kind just considered has undergone a change and that a weight has correspondingly shifted its centre of gravity, then the entropy of the body in both states is the same. For if it had become greater the transition from Z to Z' would be irreversible according to the preceding paragraph, which would contradict the initial assumption. And if it had become smaller the transition would be impossible, which would also lead to a contradiction. But if the supposed process was irreversible, then the entropy of the body in the state Z' is necessarily greater than in the state Z.

A simple illustration is given by the adiabatic expansion of a gas without the performance of external work, which was described in §§ 23 and 24. Since, for this, $dU = 0$ and $dV > 0$, we have by (72) that $dS > 0$; that is, this process is irreversible, just like friction.

§ 44. We shall now assume that the two states Z and Z' given from the outset differ owing to the different behaviour of *two* bodies, which we shall denote by 1 and 2. Let them be characterized in the state Z by the values θ_1, V_1, θ_2, V_2 and in the state Z' by the values θ'_1, V'_1, θ'_2, V'_2. Then the internal energies and the entropies of the bodies in the two states are determined, the entropies being fixed except for the arbitrary factor still involved in the definition of entropy.

To make a transition from Z to Z' possible at all we shall suppose an invariable weight G to be included in the system of bodies, the centre of gravity of G in the state Z being at the level h and in the state Z' at the level h' so that:

$$G(h - h') = (U'_1 + U'_2) - (U_1 + U_2) \quad . \quad . \quad (76)$$

The mechanical work necessary for the transition from Z to Z' is then available to exactly the right amount.

Starting from the state Z we now again endeavour to effect the transition to the state Z' by means of an irreversible process. So long as we treat each individual body adiabatically their original entropies S_1 and S_2 remain constant by (74) and we make no progress. But we have a means of altering the entropies in a reversible way. For we first bring the two bodies singly by an adiabatic reversible path to a quite arbitrary temperature θ and then put them into thermal connexion with each other (but not so that their pressures can equalize). This does not disturb the thermodynamic equilibrium, and the two bodies now represent a single system capable of certain reversible changes, and its state is determined by three mutually independent variables θ, V_1, V_2.

If we now subject this composite system to a further reversible adiabatic process by slowly altering the volumes V_1 and V_2 independently of each other in some way by compression or dilatation, the change in the total internal energy is, by the first law, equal to the total external work, thus:

$$dU_1 + dU_2 + p_1 dV_1 + p_2 dV_2 = 0$$

or, by (72):

$$N_1 dS_1 + N_2 dS_2 = 0 \quad . \quad . \quad . \quad . \quad (77)$$

In this algebraic sum the first summand denotes, by (49), the heat transferred to the first body from without while the second term denotes the heat transferred to the second body, which is equal and opposite to the former amount. Equation (77) imposes a condition on the three variables θ, V_1 and V_2, so that only two of them, say θ and V_1, may be arbitrarily chosen, while the third, V_2, is then fixed. Hence by a reversible process of this kind it is possible to bring the body 1 into any arbitrary state, whereas the state of the body 2 has necessarily to adjust itself to that of the body 1.

§ 45. But we can assert still more. Every time when the body 1 assumes its original entropy S_1 at an arbitrary temperature θ the second body 2 also possesses its original entropy S_2. For as soon as the entropy of the body 1 has again become S_1 the bodies can be separated and the body 1 can be brought alone into its initial state (θ_1, V_1) by means of a reversible adiabatic process. The state of the system of bodies which is produced in this way then differs from the original state Z only in the behaviour of the body 2; and since the whole process is reversible, the entropy of this body is, by § 43, the same as at the beginning, namely, S_2. And, indeed, corresponding to a definite value of the entropy of the body 1 there is always a perfectly definite value of the entropy of the body 2. Otherwise the general theorem of § 43 would be contradicted.

In other words, if in place of the independent variables θ, V_1, V_2 we introduce the independent variables θ, S_1 and S_2 in the equation (77), θ disappears from the equation altogether and it reduces itself to a relation of the form:

$$F(S_1, S_2) = 0$$

or, expressed in differential form:

$$\frac{\partial F}{\partial S_1} dS_1 + \frac{\partial F}{\partial S_2} dS_2 = 0 \quad . \qquad (78)$$

But in order that (77) should merge generally into (78) it is necessary and sufficient for the differential expressions of the two equations to differ only by a factor of proportionality:

$$N_1 dS_1 + N_2 dS_2 \equiv N\left(\frac{\partial F}{\partial S_1} dS_1 + \frac{\partial F}{\partial S_2} dS_2\right)$$

or:

$$N_1 = N\frac{\partial F}{\partial S_1} \text{ and } N_2 = N\frac{\partial F}{\partial S_2}$$

Consequently:

$$\frac{N_1}{N_2} = \frac{\dfrac{\partial F}{\partial S_1}}{\dfrac{\partial F}{\partial S_2}}$$

That is, the quotient of N_1 and N_2 depends only on S_1 and S_2 but not on θ. But since N_1 and N_2 are themselves determined by θ and S_2 they are necessarily of the form:

$$N_1 = f_1(S_1)\,.\,T \text{ and } N_2 = f_2(S_2)\,.\,T \quad . \quad . \tag{79}$$

respectively, where f_1 and f_2 are functions of a single argument and the function T which is the same for both bodies depends only on the temperature θ. The quantity T contains a constant arbitrary factor. We choose its value positive and fix its unit by making the difference of the values which T assumes for $\theta = 100$ and $\theta = 0$ equal to 100 thus:

$$T_{100} - T_0 = 100 \quad . \quad . \quad . \tag{80}$$

and we call the quantity T which is completely defined in this way the "absolute temperature" of the two bodies. By (72) *the absolute temperature of a body is the positive temperature function which satisfies the normalizing equation* (80) *and which when divided into the incomplete differential* $dU + pdV$ *converts it into a complete differential.* Concerning the way in which it is measured see § 49.

To complete the definition of entropy as well we bear in mind that the functions f_1 and f_2 in (79) are positive on account of the conventions about the signs of N_1, N_2 and T, but otherwise, as is clear from the discussion of § 41, they may be arbitrarily chosen. We therefore set $f_1 = 1$, $f_2 = 2$ and thus obtain from (79):

$$N_1 = N_2 = T \quad . \quad . \tag{81}$$

And from (72) we get:

$$\frac{dU + pdV}{T} = dS \quad . \quad . \quad (82)$$

or, referred to unit mass:

$$\frac{du + pdv}{T} = ds \quad . \quad . \quad . \quad . \quad (83)$$

is obtained as the entropy of a homogeneous body whose state is determined by its temperature and its volume. In the expression for the entropy there is still, as we see, an arbitrary additive constant.

§ 46. The results just obtained make it easy for us to give a complete answer to the question proposed in § 44 about the conditions governing the transition of the two bodies in question from the state Z to the state Z'. For in the reversible process described, to which the two thermally coupled bodies are subjected, we have by (77) and (81):

$$dS_1 + dS_2 = 0$$

Thus:

$$S_1 + S_2 = \text{const.} \quad . \quad . \quad . \quad . \quad (83a)$$

That is, the sum of the entropies remains constant. So if we bring the body 1 to the desired state of entropy S'_1 the body 2 acquires the entropy:

$$S^*_2 = S_1 + S_2 - S'_1 \quad . \quad . \quad . \quad . \quad (84)$$

If we then separate the two bodies and bring the volume of the first to V'_1 and its temperature to θ'_1 by means of a reversible adiabatic process, then the first body is in the desired final state and may be left out of consideration in the sequel. All that we are concerned with now is whether S^*_2 is as great, smaller than or greater than S'_2 or, what amounts to the same, by (84), whether:

$$S_1 + S_2 \overset{=}{\lessgtr} S'_1 + S'_2$$

In the first case the state Z' is fully attainable according to § 42, namely, by a reversible process; in the second case the state Z' is attainable by an irreversible process; in the third case the state Z' cannot be reached at all.

Hence the sum of the entropies of the two bodies in any state is a measure of the probability of this state.

§ 47. It now remains to generalize the last theorem for any arbitrary number of bodies. Let us imagine a system of n such bodies in two quite arbitrary states Z and Z' and enquire what is the condition that a transition from Z to Z' should be possible without changes of any sort remaining in other bodies.

In order that the transition should satisfy the energy principle we include an invariable weight in the system, whose centre of gravity in the state Z is at the level h and in the state Z' at the level h', so that:

$$G.(h-h') = (U'_1 + U'_2 + \ldots + U'_n) - (U_1 + U_2 + \ldots + U_n)$$

Starting from the state Z we now put the bodies 1 and 2 into thermal communication with each other in the manner described in § 44 and so bring the body 1 by a reversible process into the state of entropy S'_1. We then separate the two bodies and proceed in just the same way with the bodies 2 and 3 by bringing the body 2 to the state of entropy S'_2. Proceeding in the same way we bring the body $n-1$ to the state of entropy S'_{n-1}. Let the body n then have the entropy S^*_n. Since during each one of these reversible processes the total sum of all the entropies of all the bodies must on account of (83a) remain constant, we have:

$$S^*_n = (S_1 + S_2 + \ldots + S_n) - (S'_1 + S'_2 + \ldots + S'_{n-1}) \qquad (85)$$

Now each of the bodies from 1 to $n-1$ may separately be brought along a reversible adiabatic path into its desired final state. Hence the decision as to whether the state Z' is fully attainable depends on whether the entropy S^*_n of the body n is just as great, smaller than or greater than S'_n or, by (85), if we denote the sum of the entropies of all the n bodies by ΣS, whether ΣS is just as great as, smaller than or greater than $\Sigma S'$. In the first case the state Z' is attainable by a reversible process, in the second by an irreversible process, whereas in the third the transition is altogether impossible.

From this it follows conversely that *every physical or chemical process that occurs in nature takes place in such a way that the sum of the entropies of all the bodies that undergo change in the process either remains unchanged or becomes augmented.* Expressed more briefly: *the entropy is a measure of the thermodynamic probability* (§ 39).

In a reversible process the sum of the entropies remains unchanged. But the reversible processes in reality are only ideal limiting cases which are, however, of considerable importance for theoretical considerations.

The content of the second law of thermodynamics may be regarded as exhaustively described in the above sentences.

§ 48. Passing on to the applications of the second law we shall next investigate the conclusions that follow from the fact that the expression (83) for the entropy of unit mass of a homogeneous body is a complete differential. If we choose T and v as independent variables, we have:

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

and by (83):

$$ds = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\} dv$$

On the other hand:

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Consequently, since dT and dv are independent of each other:

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v \quad . \quad . \quad . \quad (86)$$

and:

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T} \cdot \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\} \quad . \quad . \quad (87)$$

If we differentiate the first equation with respect to v, and the second with respect to T we get, by equating the two expressions so obtained :

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad . \qquad (88)$$

and by (52), (86) and (87):

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \quad . \quad . \quad . \quad . \qquad (89)$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \qquad (90)$$

where c_v now denotes the specific heat referred to the absolute temperature.

By differentiating (89) with respect to v and (90) with respect to T we obtain the relation :

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad . \quad . \quad . \quad . \qquad (91)$$

which brings the connexion between the specific heat and volume into relationship with the connexion between the thermal coefficient of expansion (§ 8) and the temperature. Both quantities are very small in the case of gases.

§ 49. The relations just derived can now serve as a measure of the way in which the absolute temperature depends on any conventional temperature. So far we have had to remain satisfied with a conventional temperature θ referred to an arbitrarily chosen thermometric substance (see § 4), and it was only on grounds of expediency that in § 5 we decided in favour of using a gas as the thermometric substance. But the uniformity achieved in this way was only of a practical nature and involved no matter of principle. For, strictly speaking, all gases behave differently, particularly at high densities and low temperatures, and therefore, to be accurate, we should select some definite gas as a thermometric gas. Hence it is of the greatest importance to have a process of measurement which enables us quite generally to reduce the conventional temperature θ of a body to its absolute temperature T. In principle we can adapt *every* equation which follows from the second law for measuring T (cf. § 61 below). Let us take, for example, the equation (88) and introduce the independent variables θ and v into it in place of T and v. For it is these variables θ and v with which all measurements are effected. Since T depends only on θ, we obtain:

$$\left(\frac{\partial u}{\partial v}\right)_\theta = T\left(\frac{\partial p}{\partial \theta}\right)_v \cdot \frac{d\theta}{dT} - p$$

Here $\left(\frac{\partial u}{\partial v}\right)_\theta$, p and $\left(\frac{\partial p}{\partial \theta}\right)_v$ are to be regarded as measurable functions of θ and v. This differential equation may be integrated in the following way:

$$\int_0^\theta \frac{\left(\frac{\partial p}{\partial \theta}\right)_v d\theta}{\left(\frac{\partial u}{\partial v}\right)_\theta + p} = \int_{T_0}^{T} \frac{dT}{T} = \log T - \log T_0\,. \qquad (92)$$

and hence:

$$\log T_{100} - \log T_0 = \int_0^{100} \frac{\left(\frac{\partial p}{\partial \theta}\right)_v d\theta}{\left(\frac{\partial u}{\partial v}\right)_\theta + p} \quad . \quad . \qquad (93)$$

The last two equations together with the normalizing equation (80) determine T completely as a function of θ, and so the conventional temperature is reduced to the absolute temperature.

In particular the values of T_{100} and T_0 may be derived from (93) and (80).

In the integration on the right-hand side the volume v must clearly disappear altogether; this requirement can also be used to test the second law. The numerator of the integrand is obtained directly from the equation of state of the body, but the denominator is derived from the quantity of heat which the body takes up from without during reversible isothermal expansion or, respectively, gives up to its surroundings during reversible isothermal compression. For by equation (50) of the first law the ratio of the transferred quantity of heat q to the change of volume dv during a reversible isothermal expansion is :

$$\left(\frac{q}{dv}\right)_\theta = \left(\frac{\partial u}{\partial v}\right)_\theta + p$$

§ 50. We shall now assume in particular that θ is measured by a gas thermometer and we choose as our thermometric substance hydrogen, as in § 5. Then the coefficient of expansion α that occurs in the equation of state (9) of the gases is constant only for hydrogen; for all other gases it is different and varies with the temperature θ. Thus if we apply the last equations to any gas very simple expressions present themselves for the pressure p and the energy u, but all the simple relations that we have deduced above for gases have the disadvantage that they are qualified by the word "nearly." Not a single one of them holds rigorously. To escape from this unsatisfactory state of affairs we proceed to introduce by definition a certain type of gases, which we call "ideal gases" and which satisfy the above simple relations completely. Thus we define as the equation of state of an ideal gas the equation (9), and as the energy of an ideal gas the expression (56). We now determine the relation between the absolute temperature T and the conventional temperature θ referred to an ideal gas as the thermometric substance. By substituting the values of p and u in (92) we get after integration :

$$\log T - \log T_0 = \log (1 + \alpha\theta)$$

Thus :

$$T = T_0 + \alpha T_0 \theta \ . \tag{94}$$

Likewise, by (93) :

$$T_{100} = T_0 + 100\alpha T_0.$$

From this it follows by (80) that :

$$\alpha T_0 = 1.$$

That is, the coefficient of expansion of an ideal gas is the reciprocal of the value of the absolute temperature of the freezing point of water and hence has *the same value for all ideal gases*. Since the numerical value of α is sufficiently well known we have for the absolute temperature of the freezing point of water, by (6):

$$T_0 = \frac{1}{\alpha} = 273{\cdot}2$$

and, in general, by (94):

$$T = 273{\cdot}2 + \theta \quad . \quad . \quad . \quad . \quad (95)$$

Thus the absolute temperature is nothing more than the conventional temperature referred to an ideal gas as the thermometric substance but with the zero point displaced. Since, by definition, T is positive, we also have $\theta > -273$. The limiting point $T = 0$ is called the absolute zero of temperature. It is not attainable practically because the integral in (92) becomes infinite for it.

In future we shall as a general rule use the absolute temperature in our calculations. The equation of state of any ideal gas or of a mixture of ideal gases is then, by (35):

$$p = \frac{RnT}{V} \qquad (96)$$

where n denotes the total number of moles and R is the numerical factor which has the value (55) and which is now equally great for all ideal gases and is hence called the "absolute gas constant." Further the energy of an ideal gas is, by (56):

$$u = c_v T + \text{const.} \quad . \quad . \quad . \quad . \quad (97)$$

Although the different ideal gases satisfy the same equation of state (96) they nevertheless have different specific heats and different molar heats between which, however, the relation (55) of course always holds.

§ 51. The equation (88) together with the equation (54) of the first law in which, as always, by (95), $d\theta$

can be put in place of dT, leads to the generally valid relation:

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial v}{\partial T}\right)_p \quad . \qquad (98)$$

which may be applied to calculating c_v from c_p. Since it is not easy to measure $\left(\frac{\partial p}{\partial T}\right)_v$ in the case of solid and liquid bodies, it is advantageous to use the relation (11) here, from which:

$$c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_p^2 \quad . \qquad (99)$$

follows.

Since $\left(\frac{\partial p}{\partial v}\right)_T$ is necessarily negative, we always have $c_p > c_v$ except in the limiting case, as for water at 4° C., at which the expansion coefficient is zero, when we have $c_p = c_v$. For solid and liquid bodies the difference $c_p - c_v$ is in general relatively small, or the ratio $\frac{c_p}{c_v} = \kappa$ is only slightly greater than 1. That is, in the case of solid and liquid bodies the dependence of the energy on the temperature plays a much greater part than the volume.

The case is different with gases, as we have seen from equation (55).

§ 52. We shall now make a further application of the second law to a physical system that represents the general type of a machine which functions with a definite period and generates mechanical work from heat. The essence of such a machine consists in executing a cycle after the completion of which no other change has occurred in nature except that a certain amount of mechanical work has been performed, say in lifting a weight, and that certain bodies that serve as heat reservoirs have given up or received heat. Such a process can, for example, be carried out by a gas which experiences a series of successive adiabatic and isothermal compressions and dilatations.

During an adiabatic change the gas remains thermally isolated; during an isothermal change it is in thermal connexion with a heat reservoir at the temperature in question. The process may, however, also be connected with changes of the aggregate state or with chemical transformations; all that is essential is that the process shall be cyclical and that at the end of a period no changes shall have remained except those above mentioned. For from each of the two principal laws it is possible to derive a relation between the different changes caused by the process.

According to the first law we have for the cycle, by (39):

$$A + \Sigma Q = 0 \quad . \qquad . \qquad (100)$$

Here A denotes the sum total of the external work performed, Q the heat that has been transferred from a heat reservoir to the system under consideration during the process, the summation being extended over all heat reservoirs.

According to the second law the sum of the entropies of all the heat reservoirs becomes increased as a result of the cycle. If we assume for simplicity that the heat capacities of the reservoirs are so great that the loss of the quantity of heat Q does not appreciably alter the temperature of the reservoir, the change of entropy of the reservoir due to the loss of Q amounts, by (82) and (49), to $-\frac{Q}{T}$, since on account of the constancy of T this expression also holds for finite values of Q. Accordingly we have, by the second law, summing over all the reservoirs:

$$\sum \frac{Q}{T} \leqq 0 \qquad (101)$$

This was the first exact formulation of the second law and was due to Clausius.

We shall now consider the case of only two heat reservoirs, at the temperatures T_1 and $T_2 (> T_1)$ and shall assume that the process is a reversible cycle (CARNOT'S CYCLE). The two equations then run:

$$A + Q_1 + Q_2 = 0 \qquad (102)$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad . \qquad . \quad (103)$$

If the cycle is carried out in the direction which leads to the production of external work (raising a weight), then A, the external work done, is negative; so we set $A' = - A > 0$. Further, we see from (103) that Q_1 and Q_2 have opposite signs and that the absolute value of Q_2 is greater than that of Q_1. Now since A is negative, Q_2 is positive by (102) and Q_1 negative. So we set $Q'_1 = - Q_1 > 0$ and we can picture the result of the cycle in the following simple way. The heat reservoir 2 has given up the quantity of heat Q_2. Of this quantity the part Q'_1 has passed into the cooler reservoir 1; the other part $Q_2 - Q'_1 = A'$ has been transformed into mechanical work. Between these three positive quantities the following relations hold:

$$Q_2 : Q'_1 : A' = T_2 : T_1 : (T_2 - T_1)$$

which are entirely independent of the nature of the substance used in the process. In other words, by allowing a hotter reservoir at the temperature T_2 to give up a quantity of heat Q'_1 to a cooler reservoir at the temperature T_1 we can arrange a reversible cycle such that it enables us to obtain work:

$$A' = \frac{T_2 - T_1}{T_1} Q'_1 \quad . \qquad . \qquad (104)$$

from the hotter reservoir.

If the cyclic process is not reversible the energy equation (102) remains in force but in place of the entropy equation (103) we have the inequality:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$

which, combined with (102), gives:

$$A' = -A = Q_1 + Q_2 < Q_1 - \frac{T_2}{T_1} Q_1$$

or:

$$A' < \frac{T_2 - T_1}{T_1} \cdot Q'_1$$

Comparison with (104) shows that the work to be obtained by the transition of a quantity of heat Q'_1 at the temperature T_2 to the temperature T_1 is always less for an irreversible process than for a reversible process. Thus the latter amount, represented by (104), is the maximum amount of heat which can be obtained by means of a cyclic process with any physical system through the passage of heat Q'_1 from the hotter reservoir at the temperature T_2 to the temperature T_1.

A very special case of such a cycle is that in which heat passes directly by conduction from the hotter reservoir to the cooler reservoir. Then nothing except the two reservoirs has altered at all, and so $A = 0$. Consequently, by (100), $Q_1 + Q_2 = 0$ and by (101):

$$Q_1 \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \leqq 0$$

Hence if T_1 differs from T_2, and if Q_1 does not vanish, the sign of Q_1, the heat given up by the reservoir 1, is the same as that of $T_1 - T_2$, that is, the heat passes in the direction of the higher to the lower temperature, and the process of heat conduction is irreversible, just like friction and the process of expansion when no external work is done.

Lastly, let us apply our results to an *isothermal* cycle, otherwise arbitrary, reversible or irreversible, performed on any physical system whatsoever. Then we need consider only a single heat reservoir at the constant temperature T. The equations (100) and (101) become:

$$A + Q = 0$$

and:

$$Q \leqq 0.$$

From this it follows that $A \geqq 0$, that is, work is used up and the equivalent heat is produced in the reservoir. This inequality is the analytical expression of the impossibility of a perpetual motion machine of the second kind.

If the process is reversible the sign of inequality vanishes and both the heat Q and the work A become zero. It is due to this theorem that the second law is so fruitful when applied to reversible isothermal cycles.

§ 53. We shall now leave cyclic processes in order to deal with the general question of the direction in which any change in an arbitrarily given physical-chemical configuration occurs in nature. Let us imagine any system of bodies at the same temperature T and at the same pressure p. Let us enquire into the conditions under which a physical or a chemical change occurs in these bodies. The difference between this and our earlier discussions consists in our not necessarily assuming that the system is isolated from its surroundings. Accordingly we may not assert that its entropy necessarily increases.

For an infinitely small change of state we have by the first law:

$$dU = Q - p dV \quad . \quad . \quad . \quad . \quad (104a)$$

where U denotes the total energy, V the total volume of the system and Q the heat transferred to it from outside.

According to the second law the change in the sum of the entropies of all the bodies changed by the process is:

$$dS + dS_a \geqq 0$$

where S denotes the entropy of the system, S_a the entropy of the external bodies (atmospheric air, walls of the vessel, the liquid in the calorimeter), which we assume also to be at the temperature T. Now by (82) and (49):

$$dS_a = -\frac{Q}{T},$$

so by substituting the value of Q from (104a):

$$dS - \frac{dU + pdV}{T} \geqq 0 \ . \tag{105}$$

In this relation only such quantities occur as refer to the system in question itself; the influences of the external surroundings are completely eliminated. It represents the most general statement of the second law with regard to the occurrence of any physical or chemical change in a configuration.

It is to be observed that the inequality (105) by no means contradicts the equation (82). For the latter refers only to a physical change of state of a homogeneous body but the former to any physical or chemical change of any configuration whatsoever. Hence in general the expression (105) is an incomplete differential and cannot as a rule be integrated; that is, the second law does not allow us to make a general statement about a finite physical or chemical change of state of a system in the case where we do not know the external conditions to which the system is subject. This is really evident from the outset and holds equally well for the first law.

To arrive at a law for a finite change of state of a system we must know such external conditions as allow (105) to be integrated. Since the external conditions can be chosen at will, there are of course several of them, of which three, however, are distinguished by their special importance: firstly, we may completely isolate the system from its surroundings, keeping the volume V constant; secondly, we may keep the temperature T and the volume V constant (isothermal-isochoric process); thirdly, we may keep the temperature T and the pressure p constant (isothermal-isobaric process). We shall discuss these three cases in turn, of which each offers special points of interest.

§ 54. ISOLATED SYSTEM OF CONSTANT VOLUME. Since $Q = 0$ as well as $V =$ const., we have from the first law also that $U =$ const., and the relation (105) gives:

$$dS \geqq 0$$

That is, the entropy of the system increases. This is the formulation of the second law which has already been obtained in § 47. But we shall here make a further deduction from it. For it furnishes us directly with a sufficient condition for the stable equilibrium of the system. If, namely, the system is in the state for which its entropy has its maximum value, no further change is possible. The absolute maximum of the entropy is therefore a sufficient condition for equilibrium. This condition is not exactly necessary; for it is possible for a system to remain unchanged, although the second law would allow a change. Since the maximum of the entropy is of course fully determined by the values of U and V, we may say that the entropy S of the configuration in the case of absolute equilibrium is a definite function of U and V. The way in which it depends on U and V is shown by equation (82) from which we get:

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{106}$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} \tag{107}$$

If, in particular, we assume a single homogeneous body, we see that its entire thermodynamic behaviour is determined by expressing S as a function of U and V. For the elimination of U from the last two equations gives p as a function of T and V, and the equation (106) alone gives U as a function of T and V.

In Part Four of the present volume (§ 125) we shall become acquainted with a method of expressing S in terms of U and V; this makes it possible to solve the principal problem of thermodynamics.

Let us calculate S for the particular case of an ideal gas. From (82), (97) and (96) we get:

$$dS = \frac{C_v dT}{T} + \frac{R n dV}{V} \,. \tag{108}$$

where C_v denotes the heat capacity of the gas at constant volume. Thus:

$$S = C_v \log T + Rn \log V + \text{const.} \quad . \quad . \quad (109)$$

and by (97):

$$S = C_v \log U + Rn \log V + \text{const.} \quad . \quad . \quad (110)$$

The integration constant depends on the chemical composition of the gas; it must remain undetermined here because the differential dS in (82) refers only to changes in U and V but not to such as involve the chemical composition.

§ 55. TEMPERATURE AND VOLUME GIVEN. Since T and V are constant the relation (105) may be written in the form:

$$d\Psi \geqq 0 \qquad (111)$$

where:

$$\Psi = S - \frac{U}{T} \quad . \qquad (112)$$

So in this case, too, every change of state occurs in the sense of the growth of a definite quantity; this quantity is not now the entropy, however, but the function Ψ which is characteristic for the variables T and V. Further, we can deduce from this function results similar to those deduced in the previous section from the function S. What makes this point of view so important is the fact that the temperature T can be measured in practice much more directly than the energy U and is therefore more appropriate as the independent variable.

By (111) the sufficient condition for stable equilibrium is that the function Ψ should be a maximum. Hence in stable equilibrium the quantity Ψ is a perfectly definite function of T and V. The way in which it depends on T and V results by (112) from the complete differential:

$$d\Psi = dS - \frac{dU}{T} + \frac{U}{T^2} dT$$

or, by (82):

$$d\Psi = \frac{U}{T^2} dT + \frac{pdV}{T} \quad . \qquad (113)$$

Consequently:

$$\left(\frac{\partial \Psi}{\partial T}\right)_V = \frac{U}{T^2} \quad . \quad . \qquad (114)$$

$$\left(\frac{\partial \Psi}{\partial V}\right)_T = \frac{p}{T} \quad . \qquad (115)$$

Hence if we know the way in which the characteristic function Ψ depends on T and V, we obtain unique values of the energy and the pressure. Concerning the theoretical determination of Ψ see § 125. If we differentiate (114) with respect to V, (115) with respect to T and equate the expressions obtained, we arrive at the relation (88) already known to us. For an ideal gas we have, by integrating (113), (97) and (96), or more directly from (112) and (109):

$$\Psi = C_v \log T + Rn \log V + \frac{\text{const.}}{T} + \text{const.} \quad . \qquad (116)$$

Thus the expression for Ψ contains two undetermined constants.

§ 56. TEMPERATURE AND PRESSURE GIVEN. This case is important because it is even easier to measure the pressure than the temperature. Here the relation (105) assumes the form:

$$d\Phi \geqq 0 \, . \quad . \quad . \qquad (117)$$

where:

$$\Phi = S - \frac{U + pV}{T} = S - \frac{W}{T} \quad . \quad . \qquad (118)$$

In the latter expression we have introduced the enthalpy W (heat function at constant pressure, see § 34), by (64). Here Φ is the characteristic function and the maximum value of Φ determines the state of stable equilibrium. For the dependence of the function Φ on T and p in the state of equilibrium we get from (118):

$$d\Phi = dS - \frac{dU + pdV + Vdp}{T} + \frac{W}{T^2} dT$$

and by (82):

$$d\Phi = \frac{W}{T^2} dT - \frac{V}{T} dp \, . \qquad (119)$$

Hence:

$$\left(\frac{\partial \Phi}{\partial T}\right)_p = \frac{W}{T^2} \quad . \tag{120}$$

$$\left(\frac{\partial \Phi}{\partial p}\right)_T = -\frac{V}{T} \tag{121}$$

If we differentiate (120) with respect to p, (121) with respect to T and equate the two results, we get:

$$\left(\frac{\partial W}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{122}$$

For an ideal gas we have, by (118), (109), (96), (97) and (55):

$$\Phi = C_p \log T - Rn \log p + \frac{\text{const.}}{T} + \text{const.} \quad . \tag{123}$$

So in this case, also, two constants remain undetermined.

§ 56*a*. An example of the advantages that accrue from introducing the independent variables T and p is given by the theory of Joule and Thomson's experiment which was described in § 24; this involved the adiabatic expansion of a gas without external work being done. The theory is contained in equation (43), which, by introducing the enthalpy w of unit mass, we may write in the form $w' - w = 0$. If we now assume the difference of pressure $p' - p$ on both sides of the valve to be very small and equal to Δp, the difference in temperature $T' - T$ on both sides will also be very small ($= \Delta T$), and we then have:

$$\left(\frac{\partial w}{\partial T}\right)_p \Delta T + \left(\frac{\partial w}{\partial p}\right)_T \Delta p = 0$$

Consequently, by using (67) and (122), we get:

$$\Delta T = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{c_p} \cdot \Delta p \tag{124}$$

For an ideal gas the numerator on the right-hand side is equal to zero, and the temperature difference ΔT vanishes, as it should do. From this we see that the Joule-Thomson effect affords a very direct and delicate means of detecting deviations in the behaviour of a gas from that of an ideal gas. Actually, ΔT at ordinary temperatures and pressures is appreciably negative in the case of air. It is on this fact that the idea of Linde's method of liquefying air is founded. In the case of hydrogen ΔT is appreciably positive.

If we take as our equation of state that of van der Waals (19) we get from (124), for small values of a and b, to a first approximation :

$$\Delta T = \left(\frac{2a}{RT} - b\right) \cdot \frac{\Delta p}{c_p} \quad . \quad . \quad (125)$$

a relation which agrees approximately with the results of measurements. For most gases the expression in brackets is as in the case of air positive, which corresponds to a cooling effect, since Δp is always negative. Hydrogen is an exception because a is particularly small in its case. But by means of an appropriate preliminary cooling it is even possible in the case of hydrogen to make the first term in the bracket exceed b, the second term.

§ 57. The general relationships developed above may also be formulated in other ways. One expression which is particularly distinguished by its clarity is worth mentioning. It depends on the introduction of the function :

$$F = U - TS = -T \cdot \Psi \quad . \quad (126)$$

which, like the Ψ, may by § 55 serve as the characteristic function of the independent variables T and V. Introducing F instead of Ψ we see that the relations (114) and (115) become :

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V \quad . \quad (127)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (128)$$

By comparing (127) and (126) we see that :

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \cdot \quad (128a)$$

The quantity F is endowed with a clear meaning owing to the fact that, as we see from (126), it represents an energy. If we now consider any *isothermal* process, the general relation (105) may be written in the following form:

$$dF \leqq -pdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

or, if we integrate from any initial state to any final state denoted by a dash:

$$F' - F \leqq A \quad . \quad . \quad . \quad . \quad . \quad . \quad (130)$$

where A denotes the mechanical work performed by external forces during the process. If the isothermal process is *reversible*, the equation is:

$$F' - F = A \quad . \quad . \quad . \quad . \quad . \quad . \quad (131)$$

and a comparison with the equation (40) of the first law shows that the function F is related to the external work A in exactly the same way as the total energy U to the sum $A + Q$ of the external work and the heat received from without. This can also be expressed as follows: in a reversible process the law (40) concerning the conservation of energy resolves into two separate laws, namely the equation (131) and the supplementary equation:

$$G' - G = Q \quad . \quad . \quad . \quad . \quad . \quad (132)$$

where:

$$G = U - F = TS \quad . \quad . \quad . \quad . \quad . \quad (132a)$$

The theorem which asserts that the mechanical equivalent of the external work is independent of the path taken from the initial to the final state (§ 18) thus does not hold only for the sum $A + Q$, but also for the individual summands A and Q.

Hence, following Helmholtz, we call F the "free" energy, G the "bound" energy. The free energy F has the same meaning for the external mechanical work as the total energy U for the sum of the work and the heat. In particular we see that for a cyclic process we have not only $A + Q = 0$ but also $A = 0$ and $Q = 0$, as has already been deduced at the end of § 52.

If the isothermal process is *irreversible* the inequality:

$$F' - F < A \quad . \quad . \quad . \quad . \quad . \qquad (133)$$

holds. That is, the free energy increases less than would correspond to the external work performed, so that in this sense external work is lost. If the process occurs without external work being done, for example, at constant volume (§ 55), then $A = 0$, and:

$$F' - F < 0 \quad . \quad . \qquad . \qquad (134)$$

That is, the free energy decreases. The amount of this decrease may be regarded as a measure of the work of the forces (chemical relationship, affinity) which bring about the process; this work is lost as far as mechanical work is concerned. To find its amount we must carry out the same change in some reversible way. Then, by (131), the amount desired, $F' - F$, is actually obtained as external work A.

A particular example will make this clearer. If an aqueous solution of a non-volatile salt is diluted in some isothermal way by adding pure water, the heat of dilution can be negative or positive, according to the sign of $U' - U$, where U denotes the sum of the energies of the original solution and of the water that is to be added (initial state) and U' denotes the energy of the final solution. The external work arising from the simultaneous change of volume can always be neglected. On the other hand the difference $F' - F$ is always negative. To measure it we perform the isothermal process of dilution in some reversible way, such as the following. We first allow the water which is to be added to vaporize infinitely slowly. We then allow the vapour to expand further until the density of the vapour is equal to the density which saturated water vapour has in contact with the solution. We then bring the vapour into contact with the solution; the equilibrium is not disturbed by this step. Finally by compressing the vapour over the solution infinitely slowly we completely condense it. The whole process is reversible, and so by (131) the total external work done is equal to $F' - F < 0$; that is, work is gained (a weight is raised). This work is lost if the liquid water is added directly to the solution.

It is to be noted that all these theorems hold only for isothermal processes. The introduction of the free energy does not suffice for formulating more general laws.

In the expression (126) for the free energy the first term U as a rule easily predominates over the second term TS in chemical processes. For this reason we may often, especially in the case of low temperatures, regard the decrease of U, that is, the heat of transformation (*Wärmetönung*), instead of the decrease of F, as a measure of the chemical work; so we may enunciate the additional theorem that chemical changes always occur in the sense of decreasing U, that is, are accompanied by the generation of external heat (BERTHELOT'S PRINCIPLE). But at high temperatures where T and, in the case of gases and dilute solutions, S assume great values, the term TS can no longer be neglected without causing an appreciable error. Hence in such cases chemical changes often occur in the direction of increasing total energy, that is, heat is taken up from the surroundings.

CHAPTER IV

EQUILIBRIUM OF A SUBSTANCE IN DIFFERENT STATES OF AGGREGATION

§ 58. In the following sections we investigate the thermodynamic equilibrium of a given substance whose individual parts can belong to different states of aggregation, solid, liquid, or gaseous. Let us suppose each of these parts is physically homogeneous and is completely determined by mass, temperature and volume. For this to be so it is not necessary for the substance or even one of its parts to be chemically homogeneous (§ 22). The question of chemical homogeneity cannot even be answered with certainty. For example, it is still a very open question whether the molecules in liquid water are the same as in ice; indeed, on account of the abnormal properties of liquid water near its freezing point it is probable that the molecules even in liquid water are not all of the same kind.

We shall pursue the following line of thought. Let the substance, whose total mass M is given, be enclosed in a solid envelope of given volume V and let it be kept at a definite temperature T by being connected with a suitable heat reservoir. We set out to find the state or, if there are more, states of equilibrium, which the body can assume and to specify the conditions under which the equilibrium is stable or unstable. It is possible to carry out this investigation successfully and completely on account of the theorem deduced in § 55, which states that among all the states that can result from one another under the given conditions the most stable state of equilibrium is distinguished by having the characteristic function Ψ a maximum. In general, however, as we shall see, the quantity Ψ will be able to have several relative maxima; then, corresponding to every maximum which is not the absolute maximum there will be a more or less stable state of equilibrium. If the substance happens to be in such a state (for example, as a super-saturated vapour) then under favourable circumstances a very slight disturbance can cause the substance to pass over into another state of equilibrium, for which the corresponding value of Ψ is necessarily greater.

We have first to find those states for which the function Ψ possesses a maximum, that is, $\delta\Psi = 0$. The most general assumption we can make about the state of the substance is that three different parts of it are in the three different aggregate states. Let M_1, M_2, M_3 denote the masses of these three parts, the allocation of the suffixes being left open for the present. We then have for the total given mass:

$$M_1 + M_2 + M_3 = M \quad . \quad (135)$$

The quantities M_1, M_2, M_3 are positive or individual members may be zero.

If, further, v_1, v_2, v_3 denote the specific volumes, then the given volume is:

$$M_1v_1 + M_2v_2 + M_3v_3 = V \quad . \quad . \quad (136)$$

We now obtain for the characteristic function:

$$\Psi = M_1\psi_1 + M_2\psi_2 + M_3\psi_3$$

in which the quantities Ψ refer to unit mass.

From this we get for any infinitely small change of state:

$$\delta\Psi = \Sigma M_1\delta\psi_1 + \Sigma\psi_1\delta M_1$$

where here, as also in the sequel, the symbol Σ denotes the sum over the indices 1, 2, 3. In view of the fact that by (113) we have generally:

$$d\psi = \frac{u}{T^2}dT + \frac{p}{T}dv \quad . \quad . \quad . \quad (137)$$

we get, since $\delta T = 0$:

$$\delta\Psi = \frac{1}{T}\Sigma M_1 p_1 \delta v_1 + \Sigma \psi_1 \delta M_1 \quad . \quad . \quad (138)$$

But the variations are not all independent of one another; rather, it follows from the expressions above set down for the mass and the volume that:

$$\Sigma \delta M_1 = 0 \text{ and } \Sigma M_1 \delta v_1 + \Sigma v_1 \delta M_1 = 0$$

By means of these equations we must eliminate any two variation terms from the expression for $\delta\Psi$ in order to get purely independent variables in it. If, for example, we take the values of δM_2 and δv_2 out of the equations and substitute them in (138), we get:

$$\delta\Psi = \frac{M_1}{T}(p_1 - p_2)\delta v_1 - \frac{M_3}{T}(p_2 - p_3)\delta v_3$$
$$+ \left(\psi_1 - \psi_2 - \frac{p_2(v_1 - v_2)}{T}\right)\delta M_1 - \left(\psi_2 - \psi_3 - \frac{p_2(v_2 - v_3)}{T}\right)\delta M_3$$

Since the four variation terms that occur in this expression are completely independent of one another, each of the four coefficients must vanish individually if $\delta\Psi$ is to vanish. Accordingly we have:

$$\left.\begin{aligned} p_1 = p_2 &= p_3 \\ \psi_1 - \psi_2 &= \frac{p_1(v_1 - v_2)}{T} \\ \psi_2 - \psi_3 &= \frac{p_2(v_2 - v_3)}{T} \end{aligned}\right\} . \quad . \quad (139)$$

These four equations represent necessary properties of a state of equilibrium. Since the quantities that occur in them refer only to the internal constitution of the substance, in contrast with equations (135) and (136) which also contain the masses, we can call them the "internal" conditions of equilibrium. We shall deal with them next and shall find that they have several solutions, that is, that several states of equilibrium exist. Later (§ 65) we shall discuss the further question as to which of the different kinds of solutions furnish the most stable state of equilibrium, that is, the greatest value of Ψ for each individual case.

§ 59. First Solution. If we set:

$$v_1 = v_2 = v_3 = v$$

all four equations (139) are satisfied by these values. The three aggregate states are then identical and the whole substance is homogeneous. Since the temperature T is given from the outset the state is fully defined by the external condition (136), which in the present case runs:

$$(M_1 + M_2 + M_3)v = Mv = V$$

and gives the value of v.

This solution always has a definite meaning, but it represents a state of equilibrium only if $\frac{\partial p}{\partial v}$ is negative. If this is the case, the equilibrium is unstable or stable according to whether the function Ψ has another maximum of greater value under the given external conditions or not (cf. § 65).

§ 60. Second Solution. If we set:

$$v_1 \neq v_2 = v_3$$

the aggregate states denoted by 2 and 3 become identical and the equations (139) reduce to:

$$p_1 = p_2, \quad \psi_1 - \psi_2 = \frac{p_1(v_1 - v_2)}{T} \quad . \qquad (140)$$

In this case the substance exists in two different aggregate states together, for example, as vapour and liquid. The two equations (140) contain two unknowns v_1 and v_2; so, since p and ψ are to be regarded as known functions of T and v, these equations may serve to express v_1 and v_2, as also the pressure $p_1 = p_2$ and the values ψ_1 and ψ_2, in terms of the given temperature T. Thus the temperature completely determines the internal state of two heterogeneous parts of the same substance which are in contact and in equilibrium. The masses of the two parts are obtained from the external conditions (135) and (136), which in the present case run:

$$\left.\begin{aligned} M_1 + (M_2 + M_3) &= M \\ M_1v_1 + (M_2 + M_3)v_2 &= V \end{aligned}\right\} \quad . \quad . \quad . \qquad (141)$$

These two equations enable us to calculate M_1 and $(M_2 + M_3)$, so that the state of the system is completely determined; for in the case of the masses M_2 and M_3 only their sum is of account. Of course, the result has a physical meaning only if M_1 as well as $(M_2 + M_3)$ comes out positively.

§ 61. Let us now consider the equations (140) more closely. The first is obvious; the second may be interpreted very simply if we use as our basis the general equation of state (2) of the homogeneous substance. For, from (137) it follows by integration, since $dT = 0$, that:

$$\psi_1 - \psi_2 = \frac{1}{T}\int_2^1 pdv$$

and substituted in (140), this gives:

$$\int_2^1 pdv = p_1(v_1 - v_2) \quad . \quad . \quad (142)$$

This equation has a simple geometrical meaning, if we use the graphical method already mentioned in § 10, of representing the equation of state by means of the system of isothermals (Fig. 1). For since the integral in (142) represents the area of the surface which is enclosed by the isothermal, the x-axis and the ordinates denoted by the parts v_1 and v_2 of the isothermals, whereas on the other hand the product $p_1(v_1 - v_2)$ denotes the area of the rectangle formed by the same ordinates and the length $v_1 - v_2$ along the x-axis, the equations tell us the following.

Along every isothermal the pressure at which two aggregate states of the substance can be in equilibrium is represented by that straight line parallel to the x-axis which marks off equal areas on both sides of the isothermal (in Fig. 1 it is the straight line ABC). Thus we can derive the law of the dependence of the pressure and the density of the saturated vapour on the temperature directly from the equation of state established for homogeneous stable and meta-stable states.

Let us now consider how the internal equilibrium depends on the temperature T, the only independent variable. Differentiating equations (140) we get:

$$dp_1 = dp_2$$

$$d\psi_1 - d\psi_2 = \frac{(v_1 - v_2)dp_1}{T} + \frac{p_1(dv_1 - dv_2)}{T} - \frac{p_1(v_1 - v_2)}{T^2}dT$$

or, taking into account (137):

$$u_1 - u_2 + p_1(v_1 - v_2) = r = T(v_1 - v_2)\frac{dp_1}{dT} \tag{143}$$

where the quantity r, by (63), denotes the isothermal-isobaric heat of transformation per unit mass for a transition from the aggregate state 2 to the aggregate state 1 (heat of vaporization, heat of fusion, heat of sublimation).

This equation which was early derived from Carnot's theory (§ 31) by Clapeyron and first established rigorously by Clausius allows us among other things to calculate the heat of vaporization for any arbitrary temperature from the relation between the vapour pressure p_1 and the temperature. For example, we have for water vapour at 100° C.: $T = 273 + 100 = 373$, $v_1 = 1674$ cm.^{3}/grm., $v_2 = 1$ cm.^{3}/grm., $p_1 = 760$ mms. of mercury, $\frac{dp}{dT} = 27{\cdot}12$ mms. of mercury. Reduction to absolute units gives, by II (284):

$$\frac{dp_1}{dT} = \frac{27{\cdot}12}{760} \cdot 1013250$$

and hence by (143) the heat of vaporization is, if we divide by the mechanical equivalent of heat (42):

$$r = 539 \text{ calories/grm.}$$

which agrees excellently with the results of direct measurement.

Since all the quantities that occur in (143) can be measured fairly precisely this relation can also be used to reduce any conventional temperature θ to the absolute temperature T (§ 49). By introducing θ as the independent variable in place of T it follows from (143) that:

$$r = T(v_1 - v_2)\frac{dp_1}{d\theta}\cdot\frac{d\theta}{dT}$$

and, by integration:

$$\log T = \int\frac{v_1 - v_2}{r}\frac{dp_1}{d\theta}\cdot d\theta \quad . \quad . \quad . \quad (144)$$

from which T is to be calculated as a function of θ in the manner explained earlier.

A simple approximate formula, which in some cases gives good results but in others only moderately good results, is obtained if in equation (143) the specific volume v_2 is neglected in comparison with that of the vapour v_1 and if, in addition, the equation of state of an ideal gas is assumed to hold for the vapour. Then, by equation (96), the volume of a mole of molar weight m is:

$$V = mv_1 = \frac{RT}{p_1}$$

and the formula (143) becomes:

$$r = \frac{R}{m}\cdot\frac{T^2}{p_1}\cdot\frac{dp_1}{dT} \quad . \quad . \quad (145)$$

For example, for water at 100° C., $R = 1{\cdot}983$ in calories by (57), $m = H_2O = 18$, $T = 373$, $p_1 = 760$ mm., $\frac{dp_1}{dT} = 27{\cdot}12$ mm. as above, and hence by (145) the heat of vaporisation is $r = 547$, which is a little too large. The reason for this deviation is that the volume of the saturated water vapour at 100° C. is in reality smaller than that calculated from the gas equation (96).

The equation (143) of Carnot and Clapeyron can be applied to the process of fusion or of sublimation in the same way as to the process of vaporization. In the former case r denotes the heat of fusion of the substance, if the index 1 denotes the liquid and the index 2 the solid state; further p_1 signifies the pressure of fusion at which the solid and the liquid substances are in equilibrium with each other. The pressure of fusion, according to this, depends, like the pressure of vaporization, on the temperature, or conversely, by changing the pressure the temperature of fusion is changed :

$$\frac{dT}{dp_1} = \frac{T(v_1 - v_2)}{r} \quad . \tag{146}$$

For example, for ice at 0° C. and hence at atmospheric pressure, we get $r = 80$ calories, $T = 273$, $v_1 = 1{\cdot}000$, $v_2 = 1{\cdot}091$, and so by (146), expressing the result in atmospheres, we get:

$$\frac{dT}{dp_1} = -\ 0{\cdot}0075. \quad . \tag{147}$$

That is, by increasing the pressure by one atmosphere the melting temperature of ice is lowered by 0·0075° C., which agrees with the experimental results. For substances which, in contradistinction to ice, expand on fusion, the melting temperature is raised by increasing the pressure, so that we can say : increasing the pressure favours the aggregate state that has the smaller volume.

§ 62. The variation of the heat of transformation r with the temperature may also be calculated from our formulæ. For if we introduce the enthalpy from (65) and write (143) in the form :

$$r = w_1 - w_2$$

and differentiate with respect to T, we get, by regarding w as a function of T and p :

$$\frac{dr}{dT} = \left(\frac{\partial w_1}{\partial T}\right)_p - \left(\frac{\partial w_2}{\partial T}\right)_p + \left\{\left(\frac{\partial w_1}{\partial p}\right)_T - \left(\frac{\partial w_2}{\partial p}\right)_T\right\}\frac{dp_1}{dT} \, .$$

Taking into account (67) and (122) we obtain :

$$\frac{dr}{dT} = c_{p_1} - c_{p_2} + (v_1 - v_2)\frac{dp_1}{dT} - T\left\{\left(\frac{\partial v_1}{\partial T}\right)_p - \left(\frac{\partial v_2}{\partial T}\right)_p\right\}\frac{dp_1}{dT} \, .$$

Finally, according to (143) :

$$\frac{dr}{dT} = c_{p_1} - c_{p_2} + \frac{r}{T} - \frac{r}{v_1 - v_2}\cdot\left\{\left(\frac{\partial v_1}{\partial T}\right)_p - \left(\frac{\partial v_2}{\partial T}\right)_p\right\} \quad . \quad . \tag{148}$$

Let us again take saturated water vapour at 100° C. as an illustration. Then $T = 373$ and, in calories, $c_{p_1} = 0{\cdot}47$, $c_{p_2} = 1{\cdot}01$, $r = 539$, $v_1 = 1674$, $v_2 = 1$, $\left(\frac{\partial v_1}{\partial T}\right)_p = 4{\cdot}81$, $\left(\frac{\partial v_2}{\partial T}\right)_p = 0{\cdot}001$, from which we calculate from (148) that:

$$\frac{dr}{dT} = -\,0{\cdot}64$$

that is, the heat of vaporisation of water decreases by 0·64 calorie per degree rise of temperature.

If we again neglect v_2 in comparison with v_1 and treat the vapour as an ideal gas, the relation (148) assumes the much simpler but less exact form:

$$\frac{dr}{dT} = c_{p_1} - c_{p_2} \qquad . \qquad . \qquad (149)$$

from which we would obtain for the case in question:

$$\frac{dr}{dT} = -\,0{\cdot}54.$$

§ 63. The relation (143) may also be used for quite different purposes. As we have seen above in § 30, besides defining the specific heat at constant pressure and at constant volume we can also define any number of other specific heats according to how we regulate the external conditions under which the heating is effected. In every case the equation (51) of the first law holds.

In the case of saturated vapours interest attaches to that process of heating by which the vapour is continually kept exactly in the state of saturation. If we call the specific heat of the vapour corresponding to this process h_1—Clausius called it the "specific heat of the saturated vapour"—we obtain by (51) in our nomenclature:

$$h_1 = \frac{du_1}{dT} + p_1\frac{dv_1}{dT} \qquad . \qquad . \qquad . \qquad (150)$$

Initially we can say nothing at all about the value of h_1; in fact, we must even leave the sign of the quantity open.

For if when the temperature of the vapour is raised by 1° it is still to remain saturated, it must at any rate be simultaneously compressed, because the density of the saturated vapour increases as the temperature rises. But compression generates heat and the question arises whether this heat is not sufficiently considerable to necessitate a conduction of heat to the outside surroundings to prevent the vapour from becoming super-heated. Hence two cases are conceivable from the outset: 1. The heat of compression is so considerable that the originally saturated vapour becomes super-heated when compressed adiabatically. To maintain the state of saturation it is then necessary to conduct heat away to the outside, that is, h_1 is negative. 2. The heat of compression is too small for the compressed vapour to be kept saturated without the addition of external heat; h_1 is then positive. Between these two cases there lies the limiting case $h_1 = 0$ for which the heat of compression just suffices to maintain the vapour in the state of saturation and so the saturation curve coincides with the curve of adiabatic compression. This limiting case was assumed by James Watt, the inventor of the steam engine, to be valid for water vapour.

In contradistinction to the specific heat h_1 of the saturated vapour the specific heat of the "saturated liquid":

$$h_2 = \frac{du_2}{dT} + p_2 \frac{dv_2}{dT} \qquad (151)$$

can be directly specified numerically. For this quantity corresponds to heating a liquid in such a way that it is always kept just below the pressure of its saturated vapour. Now since the pressure, unless it amounts to many atmospheres, has no appreciable effect on the state of a liquid, the value of h_2 practically coincides with the value of the specific heat of the liquid at constant pressure, that is, we have:

$$h_2 = c_{p_2} \quad . \quad . \quad (152)$$

Subtracting equation (151) from equation (150):

$$h_1 - h_2 = \frac{d(u_1 - u_2)}{dT} + p_1 \frac{d(v_1 - v_2)}{dT}.$$

But by (143) we have, differentiating with respect to T:

$$\frac{dr}{dT} = \frac{d(u_1 - u_2)}{dT} + p_1 \frac{d(v_1 - v_2)}{dT} + (v_1 - v_2)\frac{dp_1}{dT}.$$

Consequently:

$$h_1 - h_2 = \frac{dr}{dT} - (v_1 - v_2)\frac{dp_1}{dT}$$

or, by (152) and (143):

$$h_1 = c_{p_2} + \frac{dr}{dT} - \frac{r}{T} \qquad . \qquad . \qquad (153)$$

For saturated water vapour at 100° C. we have, as above:

$$c_{p_2} = 1{\cdot}01, \ \frac{dr}{dT} = -\ 0{\cdot}64$$

$r = 539$, $T = 373$. Consequently:

$$h_1 = -\ 1{\cdot}07.$$

Thus water vapour at 100° C. represents the case 1 described above; that is, saturated water vapour at 100° C. when adiabatically compressed becomes super-heated. Or conversely, water vapour when adiabatically expanded becomes super-saturated. Other vapours exhibit the opposite effect.

§ 64. THIRD SOLUTION. If we substitute

$$v_1 \neq v_2 \neq v_3$$

in the conditions (139) that hold for internal equilibrium, these remain unaltered in the form given in § 58. This case denotes a type of equilibrium in which the substance occurs in all three states of aggregation together. The four equations (139) contain four unknowns, namely T, v_1, v_2, v_3, so that quite definite values of these four quantities correspond to them. The three aggregate states can thus exist together in equilibrium only at a certain definite temperature and for certain definite densities, and hence also only at a certain definite pressure. If we call this temperature the "fundamental temperature" we see by (139) that it is characterized by the condition that for it the pressure of the saturated vapour over the liquid is equal to the pressure of fusion or equal to the pressure of sublimation at which the solid substance is in equilibrium in contact with the gaseous substance.

As, according to the assumption we made in § 58, the temperature is given at the outset, we have two cases to distinguish. Either the given temperature is different from the fundamental temperature—this will in general be so —and then the three aggregate states cannot be in equilibrium with one another at all. Or the given temperature is equal to the fundamental temperature; then the assumed state of equilibrium is possible and the masses of the different parts of the substance can be calculated from the equations (135) and (136). But since these are only two equations, whereas there are three unknowns M_1, M_2, M_3, their values are not yet determined and an infinite number of equilibrium states of the kind in question exist, only positive values of M, however, coming into consideration.

Let us enquire, for example, into the fundamental values for water. Since at 0° C. the pressure of the saturated vapour above liquid water is 4·58 mm., but the pressure of fusion of ice is 760 mm., 0° C. is not the fundamental temperature of water. To find it we consider how the value of the saturation pressure depends on the temperature. In considering this we must observe that for every combination of two aggregate states the pressure, like the densities of the two parts of mass in contact, is determined, according to (140), by the temperature alone. We must be careful to distinguish, however, whether, for example, the saturated vapour is in contact with the liquid or with the solid substance, since the functions which represent the way in which the saturation pressure depends on the temperature come out quite differently for these two cases. The state of the saturated vapour is determined only when we know besides the temperature with what state of aggregation the vapour is in contact; and the same thing holds for the other two aggregate states. If, therefore, from now onwards we assign the suffixes 1, 2, 3 to the gaseous, liquid and solid states respectively, we must use two indices to designate a part of matter which is in the state of saturation. Of these two indices one specifies the aggregate state of the part of matter in question, the second indicates the aggregate state with which it is in contact. Thus to denote the specific volume of the saturated vapour we use the two expressions v_{12} and v_{13}, the first of which represents the vapour in contact with liquid substance, the second that in contact with solid substance. We have analogous symbols v_{23} and v_{21}, v_{31} and v_{32} for the specific volumes of the liquid and the solid substance in the state of saturation. Each of these six quantities is a definite function of the temperature alone. The corresponding pressures are: $p_{12} = p_{21}$ (pressure of vaporisation), $p_{23} = p_{32}$ (pressure of fusion), $p_{31} = p_{13}$ (pressure of sublimation). At the fundamental temperature these two pressures become equal to each other and so also to the third pressure. Thus if we express the dependence of the three pressures on the temperature by means of three curves by plotting the temperatures as abscissæ and the pressures as ordinates, the three curves intersect at a single point, the *fundamental point* F of the substance (see Fig. 4).

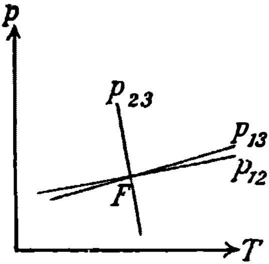

FIG. 4.

As we have already remarked, for water at 0° C. we have $p_{12} < p_{23}$. Since p_{12} increases as the temperature rises, whereas p_{23} decreases, the two pressures will coincide at a higher temperature than 0° C., but only at a very slightly higher temperature. For, by (147), p_{23} varies comparatively rapidly with the temperature, and an increase of 0·0075° C. in the temperature suffices to lower the pressure of fusion p_{23} of the ice from 760 mm. to the vapour pressure p_{12} of the water. Hence the temperature 0·0075 is very approximately the fundamental temperature of water, at which the pressures of fusion, vaporisation and sublimation coincide. From this value we then obtain the specific volumes of water vapour, water and ice as:

$$v_1 = 206{,}000, \qquad v_2 = 1{\cdot}00, \qquad v_3 = 1{\cdot}09.$$

To characterize the behaviour of a substance near its fundamental state it is expedient to establish the course of the three curves p_{12}, p_{23}, p_{31} in the neighbourhood of the fundamental point F (Fig. 4). This is done by calculating the directions in which the curves pass through F. The angles that these directions make with the x-axis are given by the differential quotients $\frac{dp_{12}}{dT}, \frac{dp_{23}}{dT}, \frac{dp_{31}}{dT}$.

Now, by (143):

$$\frac{dp_{12}}{dT} = \frac{r_{12}}{T(v_1 - v_2)}$$

and corresponding equations hold for the other two pressures. Hence we can obtain the directions of the three curves at the fundamental point as soon as we know the corresponding heat of transformation.

Let us compare, for example, the pressure p_{12} of water vapour with the pressure p_{13} of ice vapour near the fundamental temperature. Here we have, in calories: $r_{12} = 600$, $r_{13} = 80 + 600 = 680$, and so, according to the last equation, multiplying by the mechanical equivalent of heat and using the values above given for the specific volumes, we get in terms of millimetres of mercury:

$$\frac{dp_{12}}{dT} = 0{\cdot}335$$

and likewise:

$$\frac{dp_{13}}{dT} = 0{\cdot}380.$$

The curve of the sublimation pressure p_{13} thus takes a steeper course at the fundamental point F than that of the vaporisation pressure p_{12}. Or, for temperatures above the fundamental temperature (to the right of F) $p_{13} > p_{12}$, for temperatures below this temperature (to the left of F) $p_{13} < p_{12}$. Thus if we measure the pressure of saturated water vapour over water above the fundamental point and over ice below the fundamental point, the vapour pressure curve suffers a bend, whose amount is given by the sudden change of the differential quotient:

$$\frac{dp_{13}}{dT} - \frac{dp_{12}}{dT} = 0{\cdot}045.$$

For example, at − 1° C. ($dT = -1$) we get approximately:

$$p_{13} - p_{12} = -0{\cdot}045.$$

That is, at − 1° C. the pressure of ice vapour is 0·054 millimetre of mercury less than that of water vapour; a result which agrees with experimental determinations. But the existence of a sharp bend of the amount specified can be inferred only from the theory.

§ 65. Having considered the individual properties of the different possible solutions of the equations of condition that hold in the case of equilibrium we arrive at the further question as to which of these solutions has the preference in each given case, that is, which represents the most stable state of equilibrium. In view of § 58 we may formulate the question in the following brief form: given the total mass M, the total volume V and the temperature T of a substance, required to find the most stable state, that is, the absolute maximum of the characteristic function Ψ. A complete treatment of this problem would take up too much space here, so we shall give only a few of the important results. We found just above that in general the conditions of equilibrium allow three different kinds of solutions according as the substance exists in one, two or three aggregate states. Particular account, however, must be taken of the fact that the second and the third solutions have a physical meaning only if the values for the masses that result from equations (141), (135) and (136), respectively, come out positively. This limits the range of validity of the two solutions. A closer investigation further shows that within its range of validity the third solution always has the preference above the first two and that the second has the preference above the first. This may briefly be formulated as follows: the substance has the tendency to divide into its aggregate states. But this statement does not uniquely determine the state of equilibrium in all cases. For we saw in § 64 that when the substance split up into its three aggregate states an indefiniteness remained in the values of the masses M_1, M_2, M_3. The corresponding states of equilibrium are all equally stable, that is, the equilibrium is neutral. The difficulty that seems to lie in the circumstance that in nature a definite state of equilibrium always presents itself, is removed when we reflect that the occurrence of even very small fluctuations of temperature, which are inevitable, will in reality prevent the temperature which is given at the outset from permanently coinciding exactly with the fundamental temperature.

If instead of the temperature T the energy U of the substance is given the stable equilibrium will, by § 54, be characterized by the maximum of the entropy. Corresponding theorems then hold. But under no circumstances does an indefiniteness occur; rather there is always a well-defined stable state of equilibrium which is determined uniquely.

CHAPTER V

SEVERAL INDEPENDENT COMPONENTS

§ 66. We shall now investigate generally the thermodynamic equilibrium of a system consisting of different parts with common surfaces of contact in space, which, in contrast with the system treated in the preceding chapter, may be composed of any number of chemical constituents. We assume that each of the different and differently constituted parts of the system with their common boundaries in space but separated from each other by definite surfaces of contact is homogeneous (§ 22) and, following Gibbs, we call each part a "phase" of the system. For example, every aggregate state of a partially condensed substance represents a particular phase. The possible number of phases is arbitrarily great from the outset. Also we can see immediately that a system in equilibrium can have any number of solid and liquid phases but only one gaseous phase. For two different gases adjoining each other can never be in thermodynamic equilibrium with each other. If the gaseous phase is absent in the system it is called "condensed."

Besides the number of phases a characteristic of the system is the number of its "independent components," for these serve to fix the chemical constitution of the phases. We define the number of independent components of a system in the following manner. We first obtain the number of the chemically simple substances (elements) that are present in the whole system, and then exclude those substances from this series as independent substances whose quantity is determined for every phase from the outset by the quantity of the remaining substances: the number of the remaining substances is then the number of the independent components of the system. Which of the components is regarded as independent and which as dependent is a matter of indifference since we are here concerned not with the kind of the independent components but only with their number.

The question of the number of different components has nothing to do with the type of chemical combination of the individual substances in the different phases, or, in particular, with the number of different kinds of moles. For example, a quantity of water in any states of aggregation always forms a single independent component, no matter how many or how many kinds of associations and dissociations of water moles, whether as mixtures of hydrogen and oxygen or as ions, occur, so long only as the quantity of the oxygen is determined at the outset for every phase by that of the hydrogen or conversely. Whether this last assertion is actually true must, strictly speaking, be established by a special investigation. For example, as soon as we take into account the fact that water vapour at every temperature is partly dissociated into hydrogen and oxygen we obtain different proportions of the two elements H and O in the two phases of a system consisting of liquid water and water vapour, even if only complete moles of H_2O have been used to build up the system; and hence we have two independent components and not simply one.

If we denote the number of independent components of the system by α we get from the definitions set up for this number, that the state of thermodynamic equilibrium of any phase is determined by the temperature T, the pressure p and the masses of the α components contained in it, no matter whether they have finite values or are in part infinitely small. It is more convenient to choose the pressure p as the independent variable instead of the specific volume v, as was done in the previous chapter, because here the pressure in thermodynamic equilibrium is common to all phases of the system that are in free contact.

§ 67. Let us assume the total masses of the α independent components of the system as given: M_1, M_2, . . . M_α, and likewise the temperature T and the pressure p; and let us enquire into the conditions of thermodynamic equilibrium. By § 56 this is characterized by the maximum of the function Φ defined in (118); thus:

$$\delta\Phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (154)$$

holds for every change of state which is possible for a constant T and p.

Let β be the number of phases. The quantities S, U and V and hence also Φ then consist of a sum of β terms, each of which refers to an individual phase, that is, to a physically homogeneous body:

$$\Phi = \Phi' + \Phi'' + \ . \ . \ . \ \Phi^\beta \quad . \quad . \quad . \quad (155)$$

where now as well as in the sequel we distinguish the different phases by upper indices. For the first phase we then have:

$$\Phi' = S' - \frac{U' + pV'}{T} \quad . \quad . \quad . \quad . \quad (156)$$

S', U', V' and Φ' are determined by T, p and the masses M'_1, M'_2, . . . M'_α of the independent components contained in the phase. Concerning the nature of the dependence on the individual masses we can only say at the outset that if all the masses are changed in a definite ratio, for example, are doubled, each of the above quantities is changed in the same ratio. For in this change the chemical constitution of the phase remains constant; only its mass changes, this change being in exactly the ratio assumed; and the above quantities also change in the same ratio. In other words, Φ' is a homogeneous function of the first degree in the masses M'_1, M'_2, . . . M'_α (which need not of course be linear).

To express this analytically we increase all the masses in the ratio $1 + \epsilon : 1$, where ϵ is a very small number.

All changes are then very small and we get for the corresponding change of Φ' :

$$\Delta\Phi' = \frac{\partial\Phi}{\partial M'_1}\Delta M'_1 + \frac{\partial\Phi}{\partial M'_2}\Delta M'_2 + \ . \ . \ .$$

$$= \frac{\partial\Phi'}{\partial M'_1}\epsilon M'_1 + \frac{\partial\Phi'}{\partial M'_2}\epsilon M'_2 + \ . \ . \ .$$

But by our assumption we have :

$$\Delta\Phi' = \epsilon\Phi'$$

hence :

$$\Phi' = \frac{\partial\Phi'}{\partial M'_1}M'_1 + \frac{\partial\Phi'}{\partial M'_2}M'_2 + \ . \ . \ . + \frac{\partial\Phi'}{\partial M'_\alpha}M'_\alpha \quad . \qquad (157)$$

This Eulerian equation mathematically defines a homogeneous function of the first degree. The differential quotients that occur in it, for which we shall use the following abbreviations :

$$\frac{\partial\Phi'}{\partial M'_1} = \phi'_1, \ \frac{\partial\Phi'}{\partial M'_2} = \phi'_2, \ . \ . \ . \ \frac{\partial\Phi'}{\partial M'_\alpha} = \phi'_\alpha \quad . \quad . \qquad (158)$$

besides depending on T and p, depend only on the chemical constitution of the phase and not on its total mass since, if the individual masses are all changed uniformly, the numerators and denominators of the differential coefficients are changed in the same ratio.

What holds for the first phase may be immediately applied to every other phase.

By using (155) the condition of equilibrium (154) now runs :

$$\delta\Phi' + \delta\Phi'' + \ . \ . \ . + \delta\Phi^\beta = 0 \quad . \quad . \quad . \qquad (159)$$

or, since T and p are not varied, and bearing in mind (158), we get :

$$\begin{aligned} &\phi'_1\delta M'_1 + \phi'_2\delta M'_2 + \ . \ . \ . + \phi'_\alpha\delta M'_\alpha \\ &+ \phi''_1\delta M''_1 + \phi''_2 M''_2 + \ . \ . \ . + \phi''_\alpha\delta M''_\alpha \\ &+ \ . \\ &+ \phi^\beta_1\delta M^\beta_1 + \phi^\beta_2\delta M^\beta_2 + \ . \ . \ . + \phi^\beta_\alpha\delta M^\beta_\alpha = 0 \quad . \qquad (160) \end{aligned}$$

If the variations of the masses were quite arbitrary, this equation would be satisfied only if all the coefficients of the variation terms were equal to zero. But the following condition holds between the masses :

$$\left.\begin{array}{l} M'_1 + M''_1 + \;.\;.\;.\; + M_1{}^{\beta} = M_1 \\ M'_2 + M''_2 + \;.\;.\;.\; + M^{\beta}{}_2 = M_2 \\ .\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \\ M'_{\alpha} + M''_{\alpha} + \;.\;.\;.\; + M^{\beta}{}_{\alpha} = M_{\alpha} \end{array}\right\} \quad . \quad . \quad (161)$$

and so for any possible change of state :

$$\left.\begin{array}{l} \delta M'_1 + \delta M''_1 + \;.\;.\;.\; + \delta M^{\beta}{}_1 = 0 \\ \delta M'_2 + \delta M''_2 + \;.\;.\;.\; + \delta M^{\beta}{}_2 = 0 \\ .\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \\ \delta M'_{\alpha} + \delta M''_{\alpha} + \;.\;.\;.\; + \delta M^{\beta}{}_{\alpha} = 0 \end{array}\right\} \quad . \quad . \quad (162)$$

From this we get as the necessary and sufficient condition for the vanishing of the expression (160) :

$$\left.\begin{array}{l} \phi'_1 = \phi''_1 = \;.\;.\;.\; = \phi^{\beta}{}_1 \\ \phi'_2 = \phi''_2 = \;.\;.\;.\; = \phi^{\beta}{}_2 \\ .\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \\ \phi'_{\alpha} = \phi''_{\alpha} = \;.\;.\;.\; = \phi^{\beta}{}_{\alpha} \end{array}\right\} \quad . \quad . \quad (163)$$

So there are $\beta - 1$ equations for each independent component and $\alpha(\beta - 1)$ equations for all the independent components : all these equations must be fulfilled in the equilibrium state. Each of them refers to the transition of an independent component from one phase into another phase; it asserts that it is just in reference to this transition that equilibrium exists. This condition depends only on the temperature, the pressure and the internal constitution of the phases and not on their total masses : this is as it should be.

As the equations that refer to a definite component and form one row in (163) may be rearranged in any order we deduce the following theorem :—If a phase is in equilibrium with two other phases the two other phases are also in equilibrium with each other (they "co-exist"). If we combine with this the theorem already enunciated above (§ 66), that every system in equilibrium has at most a single gaseous phase, we infer that two co-existing phases, for example, two liquids which form two separate layers (water and ether) emit the same vapour. For since the one phase by hypothesis co-exists with the other phase and, of course, also with its own vapour, the other phase also co-exists with the same vapour. Hence the co-existence of solid and liquid phases can be tested by comparing their vapours.

§ 68. It is now easy to see how the state of equilibrium of the system for definite values of the temperature and pressure is determined in general from the external conditions (161) initially given and the conditions of equilibrium (163). There are α of the former and $\alpha(\beta-1)$ of the latter, so there are $\alpha\beta$ equations altogether. On the other hand the state of the β phases for given values of T and p depends on the $\alpha\beta$ masses $M'_1, \ldots M_\alpha^\beta$ of the independent components contained in them. Thus there are just as many equations as there are unknowns.

A new position arises, however, if one divides the variables on which the state of the system depends into such as concern only the internal constitution of the phases (*internal* variables, namely temperature, pressure and the ratios of the independent components) and into such as determine only the total masses of the phase (*external* variables). There are $(\alpha-1)\beta+2$ of the former, since in each of the β phases there are $\alpha-1$ mass ratios of the α independent components contained in it, and, besides, the temperature and the pressure; there are β of the latter, namely the total masses of the phases.

Now the $\alpha(\beta-1)$ equations (163) contain only internal variables, so that after these equations have been satisfied there still remain of the total number of internal variables:

$$[(\alpha-1)\beta+2]-[\alpha(\beta-1)]=\alpha-\beta+2$$

variables that are indefinite. This number cannot be negative, for otherwise the internal variables would not be sufficient to satisfy all the conditions of equilibrium (163). So we must have:

$$\beta \leqq \alpha+2 \quad . \qquad (164)$$

that is, the number of phases can exceed the number of independent components by at most 2; or, a system of α independent components can form at the most $\alpha + 2$ phases (GIBBS'S PHASE RULE).

In the limiting case, $\beta = \alpha + 2$, the number of internal variables is just sufficient to satisfy the internal conditions of equilibrium (163). Their values are then completely determined for the equilibrium state, independently of the external conditions; they form a so-called $(\alpha - 2)$-fold point. By modifying the external conditions, for example, by altering the volume, or adding heat or new quantities of substance, only the total masses of the phases but not their chemical constitution nor their temperature nor their pressure become changed. This holds until one of the phases vanishes from the system. An example for $\alpha = 1$, and hence $\beta = 3$, is given by the case, treated in the preceding chapter, of the fundamental point of a single substance, in which all three aggregate states are in contact. For $\alpha = 2$ we get $\beta = 4$, that is, a four-fold point, as, for example, an aqueous solution of common salt in contact with solid salt, ice and water vapour. In this case besides the temperature and the pressure the concentration of the solution is also fully determined.

If, further, $\beta = \alpha + 1$, the internal constitution of all phases, including temperature and pressure, depends on a single variable, which can be chosen at will, say the temperature or the pressure. This case is usually called that of "completely heterogeneous equilibrium." For $\alpha = 1$ we here have $\beta = 2$: a single independent component in two phases, for example, liquid and vapour. Both the pressure and the density of the liquid and the vapour depend only on the temperature, as has already been shown in the preceding chapter. This type of equilibrium includes vaporization when it is accompanied by chemical decomposition in so far as the system contains only a single independent component, as, for example, the vaporization of solid ammonium chloride (NH_4Cl). So long as hydrochloric acid vapour (HCl) or ammonia vapour (NH_3) is not present in excess there is a perfectly definite dissociation pressure corresponding to every temperature T. For $\alpha = 2$, we have $\beta = 3$, as, for example, when a salt solution is in contact simultaneously with its vapour and with the solid salt, or if two liquids that cannot be mixed in all proportions (water and ether) are present together with their common vapour. Vapour pressure, density and concentration in every phase are then functions of the temperature alone.

If, further, $\beta = \alpha$, the internal constitution of all the phases still depends on two variables, for example, on the temperature and the pressure. Every substance in the homogeneous state affords an illustration of $\alpha = 1$, $\beta = 1$. An example of $\alpha = 2$, $\beta = 2$ is given by a liquid solution of a salt or of an alcohol in contact with its vapour. The concentration, both in the solution and also in the vapour, is determined by the temperature and the pressure. Instead of the temperature and the pressure the concentration of the liquid solution is often taken either with the temperature or with the pressure as the two independent variables. In the first case we say that a solution of arbitrarily chosen concentration at an arbitrarily chosen temperature emits a vapour of definite tension and definite composition; in the second case we say that a solution of arbitrarily chosen concentration at an arbitrarily chosen pressure has a definite boiling point at which a vapour of definite composition is distilled off.

§ 69. As we have seen, the determination of the equilibrium state of any system depends essentially on our knowing how the characteristic function Φ for every phase of the system depends on the temperature T, the pressure p and the chemical constitution of the phase. The dependence on the temperature and the pressure is in general given by the relations (120) and (121). We have already established the expression for Φ for a gaseous phase in (123). In the case of a condensed phase (that is, liquid or solid) the pressure plays only a small part, so that we shall here need concern ourselves only with investigating the dependence on the temperature. For this the relation (120) gives the value:

$$\Phi = \int \frac{WdT}{T^2}.$$

The integration is to be performed at constant pressure. The enthalpy (Gibbs' heat function at constant pressure, § 34) is related by (67) to the heat capacity C_p at constant pressure. Thus if we integrate the last equation by parts, we get:

$$\Phi = -\frac{W}{T} + \int \frac{\partial W}{\partial T} \cdot \frac{dT}{T}$$

and, if we substitute C_p for W by (67), then:

$$\Phi = \int C_p \, . \frac{dT}{T} - \frac{1}{T} \int C_p dT \quad . \quad . \quad . \quad (165)$$

This relation reduces the characteristic function Φ directly to heat measurements. On account of the two indefinite integrals two additive constants remain undetermined in it (just as in the case of a gas in (123)) one of which has T in the denominator.

§ 70. Let us next enquire into the dependence of the characteristic function Φ of a phase on its chemical constitution. We shall first consider the question of an *ideal gaseous phase*, that is, a physically homogeneous mixture of different ideal gases. To answer this question we must, by (118), know the volume V, the energy U and the entropy S of the gas mixture. We see at once that it is better to use, instead of the individual masses of the different kinds of gases contained in the mixture, the numbers of moles of each, viz.:—n_1, n_2, n_3 . . . . For then we have simply:

$$V = \frac{RT}{p} \Sigma n_1 \quad . \quad . \quad . \quad . \quad . \quad (166)$$

The energy U of the gas mixture is obtained from the energies of the separate gases with the help of the first law. For according to this law the energy of a system remains unchanged if no external forces are exerted on it.

If we now allow any arbitrary number of gases at the same temperature and pressure to diffuse into one another isothermally and at the same pressure (along an isobar), experiment teaches us that neither the total volume is changed nor is heat taken up from without. Consequently the system retains its initial value unchanged right to the end of the process of inter-diffusion, and the energy of the mixture is equal to the sum of the energies of the separate gases before mixing, or by (97)

$$U = \Sigma n_1(c_{v_1}T + b_1) \quad . \quad . \quad (167)$$

Here, as always in the sequel, c_{v_1} does not denote the specific heat as earlier, but the molar heat at constant volume of the gas 1. The constant b_1 depends only on the nature of this gas.

We have yet to determine the entropy S of the gas mixture. Its dependence on the molar numbers n_1, n_2, n_3 . . . can be found in no other way than by applying the second law to a reversible process that is accessible to measurement and that produces a change in the ratios of the molar numbers. We may not, however, use the diffusion process above applied to determining the energy U: for this process, as we may conjecture and as is shown below, is irreversible and so leads to an inequality. On the other hand a reversible process which presents itself as suitable for our purpose is to use a "semi-permeable membrane" with the gas mixture: such a membrane can act as a partition which is permeable to one type of moles and absolutely impermeable to another type. It is true that perfect semi-permeable membranes of this kind do not exist in reality for any gases whatsoever. Indeed, it will be shown later by theory (§ 73) that in principle every gas penetrates into the substance of the membrane and will hence also diffuse through it. All that matters here, however, is that we may assume, without infringing the laws of thermodynamics, that the rate of diffusion of one kind of moles can be made *as small as we please* compared with that of another kind. This assumption is justified by the fact that the property of being semi-permeable is possessed by some substances to a very high degree of approximation in practice. For example, glowing platinum foil is permeable towards hydrogen but almost impermeable towards oxygen. The error that is incurred in setting the rate of diffusion of one type of moles equal to zero falls below any measurable limit; it resembles the error made in assuming that a salt does not absolutely vaporize or freeze out of a solution, for this assumption, too, is not rigorously true (§ 73).

By using semi-permeable membranes as partitions we shall separate the constituents of a gas mixture from one another by means of an infinitely slow reversible isothermal process of the simplest possible kind. Let a hollow cylinder (Fig. 5) be provided with four pistons in all. Of these *A* and *A′* are fixed while *B* and *B′* are movable, but in such a way that the distance *BB′* is kept constant and equal to *AA′* as is denoted by the two brackets in Fig. 5.

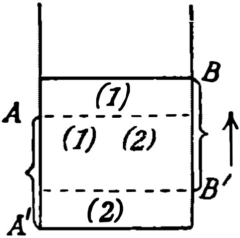

FIG. 5.

Let the base *A′* and the cover *B* of the vessel be impenetrable for all substances, while *A* and *B′* are semi-permeable, *A* being permeable only to a certain gas 1, while *B′* is permeable only to another gas 2. Above *B* the space is to be evacuated and to remain so.

Let the piston *B* be at *A* initially, so that *B′* is at *A′*, and let the enclosed space contain a mixture of the gases 1 and 2. Now let the piston *B* and hence also *B′* be raised infinitely slowly. The gas 1 flows into the space that opens up between *B* and *A*, while the gas 2 flows into the space which opens up between *B′* and *A′*. When *B′* has arrived at *A*, the two gases have been completely separated.

Let us first calculate the external work done during the process. As the upper space is evacuated the movable piston B is acted on only by the pressure of the gas 1, which moves it in the upward direction. The other movable piston is acted on only by the partial pressure of the gas 1 in the mixture in the downward direction, since the density and pressure of the gas 2 are the same on both sides of B'. But these two opposite pressures are equal in magnitude, since the presence of the piston A is of no account for the gas 1. Consequently the motion of the two rigidly connected pistons B and B' occurs without the performance of external work. Hence, if the temperature and, therefore, also the energy of the system are kept constant, no exchange of heat with the surroundings occurs.

The process, if carried out infinitely slowly, is reversible, and so the entropy in the initial state is equal to that in the final state, that is the entropy of the gas mixture is equal to the sum of the entropies of the individual gases if each alone occupies the whole volume of the mixture at the same temperature. This law may be generalized to apply to a mixture of any number of gases as follows: "the entropy of an ideal gas mixture is equal to the sum of the entropies of the individual gases, if each alone occupies the whole volume of the mixture at the same temperature." It was first enunciated by Gibbs.

The entropy of a single gas consisting of n_1 moles and at the temperature T and the pressure p is, by (109) and (96):

$$n_1\left(c_{v_1} \log T + R \log \frac{T}{p} + a_1\right)$$

where the constant a_1 depends only on the constitution of the gas but not—and this is an essential point—on the number of moles n_1, because the entropy at a definite temperature T and pressure p is proportional to the number of moles present. Instead of this expression we may also, by (55), write:

$$n_1 (c_{p_1} \log T - R \log p + a_1) \quad . \quad . \quad (167a)$$

where now c_p, like c_v, refers to a mole and not to a gramme. By Gibbs's law for the entropy of a gas mixture we get from this:

$$S = \Sigma n_1(c_{p_1} \log T - R \log p_1 + a_1) \quad . \quad (168)$$

where p_1 denotes the partial pressure (§ 9) of the moles of type 1 in the mixture.

By (15) the sum of all the partial pressures is equal to the total pressure p, and their ratios are, by (36) equal to the ratios of the numbers of moles n_1, n_2, n_3 . . . Consequently, if we denote the *concentrations* of the individual types of moles in the mixture by:

$$c_1 = \frac{n_1}{\Sigma n_1}, \quad c_2 = \frac{n_2}{\Sigma n_1}, \quad c_3 = \frac{n_3}{\Sigma n_1} \quad . \quad . \quad (169)$$

we have:

$$p_1 = c_1 p, \quad p_2 = c_2 p, \quad p_3 = c_3 p \quad . \; . \; .$$

and by (168) the entropy of the mixture is then:

$$S = \Sigma n_1 (c_{p_1} \log T - R \log (c_1 p) + a_1) \quad . \quad (170)$$

Having obtained the expression for the entropy of a gaseous mixture we are now in a position to answer the question proposed above, as to whether a diffusion process is reversible. Let us take the simplest case of the inter-diffusion of two gases, containing n_1 and n_2 moles, respectively, at constant temperature and constant pressure, hence also having constant volume and constant energy.

At the beginning of the process the entropy of the system is equal to the sum of the entropies of the separate gases, which, by (167*a*) amounts to:

$$n_1 (c_{p_1} \log T - R \log p + a_1) + n_2 (c_{p_2} \log T - R \log p + a_2).$$

When the inter-diffusion is complete the entropy of the mixture is by (170):

$$n_1 (c_{p_1} \log T - R \log (c_1 p) + a_1) \\ + n_2 (c_{p_2} \log T - R \log (c_2 p) + a_2)$$

Thus the change in the entropy of the system is:

$$- n_1 R \log c_1 - n_2 R \log c_2 \quad . \quad . \quad (171)$$

On account of (169) this is a positive quantity, from which it follows that diffusion like friction and heat conduction is an irreversible process.

At the same time we see that the increase of entropy due to diffusion depends only on the numbers of moles n_1 and n_2, but not on their nature, for example, on their molar weight. So far as the increase of entropy is concerned, then, it makes no difference whether the gases are more or less " similar " chemically. This leads us to make a strange inference. If the two gases are assumed to be identical, the increase of entropy is obviously zero, because then no change of state occurs at all. From this it follows that the chemical difference between two gases and, in fact, between any two substances at all, cannot be represented by a continuously variable quantity, so that we can speak in this case only of relations that go in steps (*sprungweise*), or of quantities that are definitely equal or unequal, as we have in the case of integers. Cf. § 13 above.

From the values found for the entropy S in (170), the energy U in (167) and the volume V in (166) the required characteristic function Φ of an ideal gas mixture comes out by (118) as :

$$\Phi = \Sigma n_1 \left(c_{p_1} \log T - R \log (c_1 p) + a_1 - c_{v_1} - \frac{b_1}{T} - R\right)$$

or, if for brevity we set the constant :

$$a_1 - c_{v_1} - R = a_1 - c_{p_1} = a'_1 \quad . \quad . \quad (172)$$

and the quantity :

$$c_{p_1} \log T - \frac{b_1}{T} - R \log p + a'_1 = \phi_1 . \quad . \quad (173)$$

which depends only on T and p and the nature of the gases but not on the number of moles, we finally get :

$$\Phi = \Sigma n_1 (\phi_1 - R \log c_1) \quad . \quad . \quad . \quad (174)$$

§ 71. We shall now take a fundamental step forward in our theory which will be of considerable practical importance. We shall assume that the expressions for

S, U, V and Φ obtained for a gaseous mixture are also valid when the numbers of moles n_1, n_2, n_3 . . . are not given constants at the outset, but are variable quantities; in other words, when the given number α of independent constituents of the system (§ 66) is less than the number of different kinds of moles. Equation (174) then gives us the value of the characteristic function Φ for all arbitrarily chosen values of the numbers of moles, and hence also for meta-stable states; the stable state of equilibrium is distinguished by having Φ a maximum. This gives us a method of calculating physical-chemical equilibrium uniquely. For if a chemical change is possible in the gaseous mixture and is such that the numbers of moles n_1, n_2 . . . simultaneously change by δn_1, δn_2 . . ., then, by § 56 equilibrium exists with respect to this change if $\delta\Phi = 0$ when $\delta T = 0$ and $\delta p = 0$. Or, by (174):

$$\Sigma(\phi_1 - R \log c_1)\delta n_1 + \Sigma n_1 \delta(\phi_1 - R \log c_1) = 0 \quad . \quad (175)$$

Since the quantities ϕ_1, ϕ_2 . . . depend only on T and p their variations are zero. Further, we have:

$$n_1 \delta \log c_1 + n_2 \delta \log c_2 + \ . \ . \ . = \frac{n_1}{c_1}\delta c_1 + \frac{n_2}{c_2}\delta c_2 + \ . \ . \ .$$

and, by (169):

$$= \Sigma n_1 . (\delta c_1 + \delta c_2 + \ . \ . \ . \ ) = \Sigma n_1 . \delta(c_1 + c_2 + \ . \ . \ . \ ) = 0.$$

Hence there remains of the condition for equilibrium:

$$\Sigma(\phi_1 - R \log c_1)\delta n_1 = 0.$$

Since only the ratios of the variations δn_1, . . . are important in this equation, we set

$$\delta n_1 : \delta n_2 : \ . \ . \ . = \nu_1 : \nu_2 : \ . \ . \ . \ . \quad (176)$$

where we take ν_1, ν_2, . . . to stand for simple positive or negative integers, namely moles that combine or decompose during the chemical change under consideration. The condition for equilibrium then runs:

$$\Sigma(\phi_1 - R \log c_1)\nu_1 = 0 \quad . \quad . \quad (177)$$

or:

$$\nu_1 \log c_1 + \nu_2 \log c_2 + \ldots = \frac{\nu_1\phi_1 + \nu_2\phi_2 + \ldots}{R} = \log K \,. \qquad (178)$$

Since the right-hand side of the equation, log K, depends, by (173), only on T and p, the equation gives a definite characteristic relation between the concentrations of the different kinds of moles, if T and p are given. This relation may also be written in the form:

$$c_1^{\nu_1} c_2^{\nu_2} c_3^{\nu_3} \ldots = K \,. \qquad . \quad . \quad (179)$$

From this we see that at finite temperatures and finite pressures none of the concentrations can be zero, or, in other words, that in the gas mixture all the kinds of moles possible at all are present in finite quantity even if only to a very small extent. So, for example, in water vapour even at low temperatures there is always a small amount of uncombined hydrogen and oxygen (cf. also § 66 below). For many phenomena this circumstance is of course, of no importance.

The relation between the equilibrium constants K and the temperature and pressure is, by (178) and (173) of the form:

$$K = \frac{A e^{-\frac{B}{T}} T^c}{p^{\nu_1 + \nu_2 + \ldots}}$$

or:

$$\log K = \log A - \frac{B}{T} + C \log T - (\nu_1 + \nu_2 + \ldots) \log p \quad (180)$$

where we have used the abbreviations:

$$\left.\begin{array}{llll} \nu_1 a'_1 & + \nu_2 a'_2 & + \ \ldots & = R \log A \\ \nu_1 b_1 & + \nu_2 b_2 & + \ \ldots & = RB \\ \nu_1 c_{p_1} & + \nu_2 c_{p_2} & + \ \ldots & = RC \end{array}\right\} . \quad . \quad (181)$$

From this we can derive a close relation between the value of K, the heat tone (*Wärmetönung*) and the change of volume that present themselves during the chemical change in question.

For, by (180), we have for any change of T and p :

$$d \log K = \left(\frac{B}{T^2} + \frac{C}{T}\right) dT - (\nu_1 + \nu_2 + \ . \ . \ . \ ) \frac{dp}{p} \ . \qquad (182)$$

Now by the first law (62) we have for the quantity of heat which must be transferred to the system from without during any isobaric change of state :

$$Q = U' - U + p(V' - V)$$

and so for the isothermal-isobaric change characterized by the numbers ν we have by (167), (166) and (55) :

$$T \Sigma \nu_1 c_{p_1} + \Sigma \nu_1 b_1 = R(CT + B) = r \ . \quad . \qquad (183)$$

and correspondingly by (166) for the volume change which occurs during the same isothermal-isobaric change :

$$\frac{RT}{p} (\nu_1 + \nu_2 + \ . \ . \ . \ ) = v \qquad . \qquad (184)$$

By comparison with (182) this gives:

$$\frac{\partial \log K}{\partial T} = \frac{1}{R} \cdot \frac{r}{T^2} \qquad . \qquad . \quad . \qquad (185)$$

and:

$$\frac{\partial \log K}{\partial p} = - \frac{1}{R} \frac{v}{T} \qquad . \quad . \quad . \qquad (186)$$

Thus by measuring the heat tone and the corresponding change of volume we can determine how the equilibrium state depends on the temperature and the pressure. For a thermally neutral reaction ($r = 0$) the equilibrium is independent of the temperature, and if the volume is not changed by the transformation ($v = 0$) the equilibrium is independent of the pressure, as may also be seen directly from (180), because the change of volume is proportional to the change in the total number of moles.

§ 72. As for the ideal gaseous phase so also for any arbitrary other phase the function Φ, which is the characteristic function for thermodynamic equilibrium, can be found as a function of T, p and the numbers of moles n_1, n_2 . . . by determining V, U and S. But, as we may well expect, the expressions for these quantities are in general found to be fairly complicated. They become relatively simple, however, for the case now to be considered, which represents the phase of a *dilute solution*, that is, a phase in which a definite kind of moles far exceeds in number all the other kinds of moles. We call this kind of moles the "solvent" and denote the number of moles in it by n_0; all the others are called "dissolved substances" (or solutes) and the number of their moles is denoted by n_1, n_2, n_3 . . . . Then, according to our assumption, n_0 is very large compared with the sum $n_1 + n_2 + n_3 + \dots$. The aggregate state of the solution is immaterial; it can be solid, liquid or gaseous.

The reason for the great simplification in the case of a dilute solution is founded on the mathematical theorem that a function of *small* variables, which is finite and continuous and has finite and continuous differential coefficients, is necessarily a linear function of these variables. This allows us to specify the way in which U and V depend on n_0, n_1, n_2 . . . from the very outset. In physical language this means that, apart from the actions of the moles of the solvent on one another, the properties of a dilute solution necessarily depend only on the mutual actions between the moles of the solvent and the moles of the dissolved substances, but not on the actions of the dissolved substances on each other; for the latter are small quantities of a higher order.

In actual fact let us first consider the energy U of the solution and let us form the quotient of U and n_0, the number of moles of the solvent. Since U is a homogeneous function of the first degree in the number of moles, this quotient will remain unaltered if all the numbers of moles of each kind n_0, n_1, n_2 . . . are changed in the same ratio, that is, it is a function of the ratios $\frac{n_1}{n_0}$, $\frac{n_2}{n_0}$, . . .; and since these ratios are all small, it is a linear function:

$$\frac{U}{n_0} = u_0 + u_1 \frac{n_1}{n_0} + u_2 \frac{n_2}{n_0} + \dots$$

in which the quantities u_0, u_1, u_2 . . . do not depend on the numbers of moles of each kind, but only on the temperature T, the pressure p and the nature of the kinds of moles present in the solution; and, indeed, in such a way that u_0 depends only on the nature of the solvent, whereas u_1 depends only on the nature of the solvent and the first dissolved substance, and so forth. Thus u_0 corresponds to the mutual actions of the moles of the solvent on one another, u_1 on those of the solvent with the moles of the first dissolved substance and so forth.

A fully analogous argument applies to the volume V of the solution. Thus we have:

$$\left.\begin{aligned} U &= n_0u_0 + n_1u_1 + n_2u_2 + \ldots \\ V &= n_0v_0 + n_1v_1 + n_2v_2 + \ldots \end{aligned}\right\} \quad . \qquad (187)$$

We regard these formulæ, exactly like the corresponding expressions for a gaseous phase, as valid for other cases besides that for which the numbers of moles n are given constants, that is, for others besides the thermodynamic states of equilibrium (cf. § 71). They may be tested by actual measurement. For if we dilute the solution still further, by adding say a mole of the solvent by, say, an isothermal-isobaric process, then by means of the last equations just above we may calculate the resulting heat of transformation and change of volume, provided that the numbers n remain constant.

A mole of the pure solvent, taken always at the same temperature and pressure, has the volume v_0 and the energy u_0. After the dilution has been effected the volume of the solution has become:

$$V' = (n_0 + 1)v_0 + n_1v_1 + n_2v_2 + \ldots$$

and the energy has become:

$$U' = (n_0 + 1)u_0 + n_1u_1 + n_2u_2 + \ldots$$

The increase of volume caused by the dilution is obtained by subtracting the sum of the original volume V of the solution and the volume of one mole of the pure solvent from the final volume V'; thus $V' - (V + v_0)$. That is, the increase of volume is nil. The heat transferred from without is, by the first law (62) :

$$Q = U' - (U + u_0) + p\,(V' - (V + v_0))$$

and likewise vanishes.

In drawing these conclusions it is assumed that the numbers of moles of the dissolved substances, $n_1, n_2 \ldots$ remain unchanged during the process of dilution, that is, that no chemical changes occur. We may accordingly enunciate the following theorem :—A dilute solution has the property that further dilution, so long as no chemical changes are produced by it in the dissolved substances, causes neither an appreciable increase of volume nor appreciable heat of transformation (*Wärmetönung*). Conversely, every change of volume or heat of transformation that occurs when a dilute solution is further diluted must be ascribed to a chemical change among the dissolved substances.

We now proceed to calculate the entropy S of a dilute solution as a function of the independent variables T, p, $n_0, n_1, n_2 \ldots$. By (82) we have, provided the numbers of moles $n_0, n_1, n_2 \ldots$ are kept constant :

$$dS = \frac{dU + pdV}{T}$$

and by (187) :

$$dS = n_0\frac{du_0 + pdv_0}{T} + n_1\frac{du_1 + pdv_1}{T} + n_2\frac{du_2 + pdv_2}{T} + \ldots$$

Now since the u's and the v's depend only on T and p, but not on the n's, the coefficients of $n_0, n_1, n_2 \ldots$ must also separately be complete differentials, that is, there must be certain variables s, which depend only on T and p, and such that :

$$\left.\begin{aligned} ds_0 &= \frac{du_0 + pdv_0}{T} \\ ds_1 &= \frac{du_1 + pdv_1}{T} \\ &\ldots\ldots\ldots\ldots \end{aligned}\right\} \quad . \quad . \qquad (188)$$

We then have:

$$S = n_0 s_0 + n_1 s_1 + n_2 s_2 + \ . \ . \ . + C \ . \quad . \qquad (189)$$

where the integration constant C is independent of T and p but may, however, depend on the numbers of moles present.

Hence if for any particular value of the temperature and the pressure we know how C depends on the numbers of moles, this value of C is also its general value for *any* temperature and pressure.

We proceed to calculate C as a function of the n's for the special case when the temperature is high and the pressure is low. If the temperature is sufficiently raised and the pressure sufficiently lowered, the solution, no matter what its aggregate state may be initially, will transform completely into the gaseous state. In reality this will be accompanied by chemical changes and changes of the aggregate state, that is, the numbers of moles, n, will change, the phases will split up and so forth. For in nature only such states can be realized as lie fairly close to stable states of equilibrium. Here, however, we wish to, and indeed are compelled to, assume that the process is such that all the numbers of moles n remain unchanged and that the whole configuration always forms only a single phase; for it is only then that the quantity C retains its value. This assumption is allowed because the numbers of moles n together with T and p form the independent variables of the system. Cf. the comment on (187). Such a process can only be imagined since it passes through meta-stable states; but there is no objection to its use, since the above expressions for V, U and S are valid not only for stable states but for all states which are characterized by arbitrary values of the independent variables T, p, n_0, n_1, n_2 . . . . For the stable state of equilibrium arises from the general states as a particular case in consequence of a special condition which is to be set up below.

Since when the temperature has been sufficiently raised and the pressure sufficiently lowered, every gaseous phase assumes so small a density that it may be regarded as a mixture of ideal gases (see end of § 17) the expression (189) for the entropy must here transform into (170); it must be carefully noted that the moles constituting the first kind are denoted by the index 0. But this transition, during which the values of the n's remain constant, is possible only if the integration constant C in (189) is identical with that additive term in (170) which is independent of T and p. Thus:

$$C = -R(n_0 \log c_0 + n_1 \log c_1 + \ldots) \quad . \quad (190)$$

where the concentrations are:

$$c_0 = \frac{n_0}{n_0 + n_1 + n_2 + \ldots}, \; c_1 = \frac{n_1}{n_0 + n_1 + n_2 + \ldots} \quad \ldots \quad (191)$$

Hence, by (189) the entropy of a dilute solution for any arbitrary temperature and pressure is:

$$S = n_0(s_0 - R \log c_0) + n_1(s_1 - R \log c_1) + \ldots \quad . \quad (192)$$

If we further use the following abbreviations for the quantities which depend only on T and p but not on the n's:

$$\left.\begin{array}{l} s_0 - \dfrac{u_0 + pv_0}{T} = \phi_0 \\ s_1 - \dfrac{u_1 + pv_1}{T} = \phi_1 \\ s_2 - \dfrac{u_2 + pv_2}{T} = \phi_2 \\ \ldots\ldots\ldots\ldots \end{array}\right\} \quad \ldots \quad (193)$$

then, by (118), (192) and (187), the characteristic function Φ of the solution finally becomes:

$$\Phi = n_0(\phi_0 - R \log c_0) + n_1(\phi_1 - R \log c_1) + \ldots \quad . \quad (194)$$

This concludes the determination of the thermodynamic properties of a dilute solution.

§ 73. We shall now proceed to set up the condition of equilibrium for a system consisting of *any* number of phases. As regards notation, we shall as before distinguish the different groups of moles in one and the same phase by means of suffixes but the different phases will be distinguished by dashes, the first phase being left for the sake of simplicity without a dash. The whole system is then represented by the symbol :

$$n_0m_0, n_1m_1, n_2m_2, \ldots \mid n'_0m'_0, n'_1m'_1, n'_2m'_2, \ldots \mid n''_0m''_0, n''_1m''_1, n''_2m''_2, \ldots \mid \ldots \quad (195)$$

The numbers of moles are denoted by n's, their individual weights by m's, and the individual phases are separated by vertical lines. In the general formulæ we denote the summations over the different kinds of moles in one and the same phase by noting down the individual terms of the summation; but the summing over the different phases is denoted as usual by the symbol Σ.

To be able to apply the expressions above derived we shall assume that every phase represents either a mixture of ideal gases or a dilute solution. The latter is true even in the case when the phase contains only one kind of mole, as, for example, a chemically homogeneous precipitate from a solution. For one kind of mole taken alone is a dilute solution in which the concentrations of the dissolved substances are all equal to zero.

Let us suppose that the system (195) can be subjected to an isothermal-isobaric change such that the numbers of moles $n_0, n_1, n_2 \ldots$, $n'_0, n'_1, n'_2 \ldots$ change simultaneously by the amounts δn_0, δn_1, $\delta n_2 \ldots$, $\delta n'_0$, $\delta n'_1$, $\delta n'_2 \ldots$ Then, by § 56, equilibrium persists for this change if, T and p being constant, we have $\delta\Phi = 0$, or, by (194), if :

$$\Sigma(\phi_0 - R\log c_0)\delta n_0 + (\phi_1 - R\log c_1)\delta n_1 + \ldots$$
$$+ \Sigma n_0\delta(\phi_0 - R\log c_0) + n_1\delta(\phi_1 - R\log c_1) + \ldots = 0$$

The summation Σ is to be performed over all the phases. The second row vanishes identically for the same reason as was given in § 71 for the case of a single gaseous phase.

If we again introduce the simple integral ratios that are characteristic of the change in question:

$$\delta n_0 : \delta n_1 : \delta n_2 \; . \; . \; . \; : \delta n'_0 : \delta n'_1 : \delta n'_2 : \; . \; . \; .$$
$$= \nu_0 : \nu_1 : \nu_2 \; . \; . \; . \; : \nu'_0 : \nu'_1 : \nu'_2 : \; . \; . \; . \qquad (196)$$

the condition of equilibrium runs:

$$\Sigma(\phi_0 - R \log c_0)\nu_0 + (\phi_1 - R \log c_1)\nu_1 + \; . \; . \; . = 0$$

or:

$$\Sigma\nu_0 \log c_0 + \nu_1 \log c_1 + \; . \; . \; . = \frac{1}{R}\Sigma\nu_0\phi_0$$
$$+ \nu_1\phi_1 + \; . \; . \; . = \log K \quad . \quad . \quad (197)$$

The equilibrium constant K depends, like the quantities ϕ, not on the numbers of moles but only on the temperature, the pressure and the nature of the constituents of the different moles. Its dependence on T and p comes out of its definition:

$$d(\log K) = \frac{1}{R}\Sigma\nu_0 d\phi_0 + \nu_1 d\phi_1 + \; . \; . \; . \qquad (198)$$

Now, by (193) we have:

$$d\phi_0 = ds_0 - \frac{du_0 + pdv_0 + v_0dp}{T} + \frac{u_0 + pv_0}{T^2}dT$$

and, on account of (188):

$$d\phi_0 = -\frac{v_0dp}{T} + \frac{u_0 + pv_0}{T^2}dT.$$

Likewise:

$$d\phi_1 = -\frac{v_1dp}{T} + \frac{u_1 + pv_1}{T^2}dT$$

. . . .

Consequently, by substituting in (198):

$$\frac{\partial \log K}{\partial T} = \frac{1}{RT^2}\Sigma(\nu_0 u_0 + \nu_1 u_1 + \; . \; . \; .) + p(\nu_0 v_0 + \nu_1 v_1 + \; . \; . \; .)$$

$$\frac{\partial \log K}{\partial p} = -\frac{1}{RT}\Sigma\nu_0 v_0 + \nu_1 v_1 + \; . \; . \; .$$

In these equations the sums Σ taken over all the phases denote, by (187), nothing other than the heat of transformation r represented by (62) and the volume change v, which occur during the isothermal-isobaric process here characterized by the numbers ν. Hence we have :

$$\frac{\partial \log K}{\partial T} = \frac{r}{RT^2} \quad . \qquad . \quad (199)$$

$$\frac{\partial \log K}{\partial p} = -\frac{v}{RT} \quad . \qquad . \quad . \quad (200)$$

which are exactly the same relations as (185) and (186) which were found above for a mixture of ideal gases.

The elimination of K from the last two equations leads to a general relationship between the heat of transformation r and the change of volume v :

$$\frac{\partial r}{\partial p} = v - T\frac{\partial v}{\partial T} \quad . \quad . \quad . \quad . \quad . \quad (201)$$

which can also be derived directly from (122).

By means of equation (197) it is possible to set up for every thermodynamic system exactly as many conditions of equilibrium as there are possible kinds of transformations, the constant of equilibrium K having of course a different value in each case. This corresponds fully with the requirements of Gibbs's Phase Rule. For we must carefully distinguish the numbers of different kinds of moles of a phase from the number of its independent components (§ 66). Both numbers determine the mass and the chemical constitution of the phase but the former does this quite generally while the latter does so only on the assumption that the phase is in thermodynamic equilibrium. That is why the latter alone, as we saw in § 68, is of importance for Gibbs's Phase Rule. For when a new kind of moles is taken into account, then although the number of variables is increased, the number of possible transformations increases at the same time and hence also the number of conditions of equilibrium.

The equation (197) tells us further that in the state of equilibrium all the kinds of moles that are at all possible in the system are represented in every individual phase to a finite degree of concentration; as otherwise the corresponding logarithm would become negative. This also means, for example, that in a solid precipitate thrown down by an aqueous solution water moles always occur or that in the case of a solution some salt always evaporates together with the solvent. This view, which seems strange at first sight, receives support in various ways; for example, it accounts for the fact that neither a gas nor a liquid nor a solid body can ever be completely freed from the last traces of foreign contaminating substances. It also proves that there can be no such thing as a semi-permeable partition in the absolute sense (cf. § 70). This does not, of course, prevent our ascribing an arbitrary small value to the concentration of a dissolved substance.

The above discussion is based on the assumption that the equilibrium constant K has a finite value which depends only on the temperature and the pressure. But if the temperature T approaches the absolute zero, a glance at equation (199) informs us that, provided the heat of transformation r of the change in question remains finite, the quantity $\log K$ assumes, when the temperature decreases to an indefinitely small value, an infinite value, positive or negative according to the direction of the reaction indicated by the signs of the numbers ν. By (197) it follows from this that at the absolute zero of temperature the reaction continues until it is fully completed, the concentrations of the moles that become transformed in the process becoming equal to zero.

This result agrees with the general deduction made in § 57 that Berthelot's Principle holds *at low temperatures.* This principle states that chemical transformations always proceed in the direction in which the greatest possible amount of heat is generated, that is, until all the kinds of moles that are richer in energy have been completely used up.

§ 74. Some particularly interesting applications of the condition of equilibrium (197) will now be discussed. Firstly we consider the case, already treated in the previous chapter, of a single independent component in two aggregate states, as this brings out very clearly the peculiarities of the method here used. The system consists of two phases, say a liquid and a gaseous or a solid phase. By (195) the symbol of the system is:

$$n_0 m_0 \,|\, n'_0 \, m'_0.$$

Let each phase contain only a single kind of mole; but the moles in both phases need not be the same.

If a liquid mole vaporizes or solidifies, then, in our new notation:

$$\nu_0 = -1, \;\; \nu'_0 = \frac{m_0}{m'_0}$$

$$c_0 = \frac{n_0}{n_0} = 1, \;\; c'_0 = \frac{n'_0}{n'_0} = 1$$

and consequently the condition of equilibrium (197) becomes:

$$0 = \log K = -\phi_0 + \frac{m_0}{m'_0}\phi'_0 \qquad . \qquad (202)$$

Since K depends only on T and p, this equation expresses a definite relation between p and T: the law of the dependence of the vaporization pressure or fusion pressure on the temperature, or the converse. The actual content of this law becomes clear if we take into account the dependence of K on p and T. For if we differentiate the last equation totally, we get:

$$\frac{\partial \log K}{\partial T} dT + \frac{\partial \log K}{dp} dp = 0$$

or, by (199) and (200):

$$\frac{r}{T^2} dT - \frac{v}{T} dp = 0.$$

Now the volume change of the system in the change in question is, in our present notation:

$$v = \nu_0 v_0 + \nu'_0 v'_0 = \frac{m_0}{m'_0} v'_0 - v_0$$

Consequently:

$$r = T\left(\frac{m_0}{m'_0} v'_0 - v_0\right)\frac{dp}{dT}$$

or, referred to unit mass :

$$\frac{r}{m_0} = T\left(\frac{v'_0}{m'_0} - \frac{v_0}{m_0}\right)\frac{dp}{dT}$$

which is identical with the Carnot-Clapeyron formula (143).

§ 75. **Two independent components in a phase.** According to the Phase Rule the pressure and temperature are not the only variables in this case ; there is another, for example the quantity of dissolved substance in 1 litre of the solution. The concentration of any kind of mole is then determined for the equilibrium state, no matter whether the mole is produced by dissociation, association, hydration or hydrolysis. Consider the simple case of the electrolytic dissociation of a binary electrolyte, for example, acetic acid in water. If the theory is to be applicable we must assume that the electrolyte is weak, that is, that in the expression for the energy and the volume of the solution we may neglect the actions which the ions exert on one another in virtue of their charges. For it is only under this condition that the equations (187) are valid.

The symbol of the system is :

$$n_0 m_0,\ n_1 m_1,\ n_2 m_2,\ n_3 m_3$$

where n_1 denotes the number of undissociated moles and $n_2 = n_3$ the number of dissociated moles. The total number of moles is :

$n = n_0 + n_1 + n_2 + n_3$ (which only slightly exceeds n_0.)

The concentrations are :

$$c_0 = \frac{n_0}{n},\ c_1 = \frac{n_1}{n},\ c_2 = c_3 = \frac{n_2}{n}.$$

The transformation in question consists in the dissociation of a dissolved mole, thus :

$$\nu_0 = 0,\ \nu_1 = -1,\ \nu_2 = \nu_3 = 1.$$

Accordingly we have, by (197), in the equilibrium state :

$$-\log c_1 + 2\log c_2 = \log K$$

or:

$$\frac{c_2^2}{c_1} = K \quad . \qquad . \qquad (203)$$

which is the law, first enunciated by Ostwald, for the dilution of a binary electrolyte.

§ 76. **Two independent components in two phases.** According to the Phase Rule the equilibrium state is determined by two variables, such as the temperature and pressure, or concentration of a phase and temperature or pressure. To get a better survey of this wide field of phenomena it is found advantageous to consider the special case where the second of the two phases contains only a single component in appreciable quantity. This case sub-divides further into two subordinate cases which are to be well distinguished; they result according as the component that alone occurs in the second phase forms the solute or the solvent in the first phase. We treat these two subordinate cases in succession, beginning with that in which *the component that occurs isolated in the second phase forms the solute in the first phase.* An illustration of this is given by the absorption of a gas, say carbon dioxide, in a liquid of comparatively inappreciable vapour pressure, say water at a low temperature. By (195) the symbol of the system is:

$$n_0 m_0, \; n_1 m_1 \mid n'_0 m'_0.$$

We leave open the possibility of the dissolved mole m_1 being a multiple of the free gaseous mole m'_0. The concentrations of the different kinds of moles of the system in the two phases are:

$$c_0 = \frac{n_0}{n_0 + n_1} \qquad c_1 = \frac{n_1}{n_0 + n_1} \qquad c'_0 = \frac{n'_0}{n'_0} = 1.$$

The transformation in question consists in the vaporization of a dissolved mole, thus:

$$\nu_0 = 0, \; \nu_1 = -1, \; \nu'_0 = \frac{m_1}{m'_0}.$$

Hence the condition of equilibrium (197):

$$\nu_0 \log c_0 + \nu_1 \log c_1 + \nu'_0 \log c'_0 = \log K$$

becomes:

$$-\log c_1 = \log K \quad . \quad . \quad . \quad . \quad (204)$$

That is, for a definite temperature and a definite pressure (which also determines K) the concentration c_1 of the gas in the solution also assumes a definite value. The dependence of the concentration on the pressure and the temperature is obtained by substituting the last equation in the equations (199) and (200). This gives:

$$\frac{\partial \log c_1}{\partial T} = -\frac{1}{R}\frac{r}{T^2} \quad . \qquad (205)$$

$$\frac{\partial \log c_1}{\partial p} = \frac{1}{R}\frac{v}{T} \quad . \quad . \qquad (206)$$

where r is the amount of heat to be taken up from the surroundings during the isothermal-isobaric vaporization of a mole of liquid, v being the resulting increase of volume. Now, since v represents to a close approximation the volume of $\nu'_0 = \frac{m_1}{m'_0}$ gaseous moles, we may, by (96), set:

$$v = \frac{m_1}{m'_0}\frac{RT}{p}$$

and the equation (206) gives:

$$\frac{\partial \log c_1}{\partial p} = \frac{m_1}{m'_0} \cdot \frac{1}{p}.$$

Integrating, we get:

$$c_1 = C \,.\, p^{\frac{m_1}{m'_0}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (207)$$

That is, the concentration of the dissolved gas in the liquid is proportional to that power of the pressure which denotes the degree of association of the gaseous moles in the liquid. Thus if the dissolved quantity of gas is proportional to the pressure (Henry's Law; also known as the Bunsen–Henry Law on the Continent), as in the case of the absorption of carbon dioxide in water, it follows that the mole of carbon dioxide dissolved in the water is identical with the gaseous mole.

The factor of proportionality C, which gives us a measure of the solubility of the gas, also depends on the temperature; the manner of its dependence is derived from (205) combined with (207), which gives:

$$\frac{\partial \log C}{\partial T} = -\frac{1}{R}\frac{r}{T^2} \quad . \quad . \quad . \quad . \quad (208)$$

Thus if the gas escapes from the solution owing to the addition of heat from outside, as in the case of carbon dioxide in water, then $r > 0$ and the solubility decreases as the temperature increases. Conversely the heat of transformation during the process of absorption can be calculated from the variation of C with the temperature.

§ 77. **The component which occurs alone in the second phase forms the solvent in the first phase.** This case is realized when a pure solvent separates out from a solution which is in any arbitrary aggregate state, and passes over into any other aggregate state during the process, such as by freezing, vaporizing, melting or subliming. The general type of such a system is, by (195):

$$n_0 m_0,\ n_1 m_1,\ n_2 m_2,\ n_3 m_3,\ \ldots \mid n'_0 m'_0.$$

The nature and the number of the different kinds of moles which form the solute in the solution are left quite open; and likewise the question as to whether the moles of the solvent have the same or different weights in the two phases. The sum of all the moles in the solution is:

$n = n_0 + n_1 + n_2 + \ldots$ (which only slightly exceeds n_0).

The concentrations of the different kinds of moles are:

$$c_0 = \frac{n_0}{n},\ c_1 = \frac{n_1}{n},\ c_2 = \frac{n_2}{n},\ \ldots\ c'_0 = \frac{n'_0}{n'_0} = 1.$$

A possible change is the transition of a mole of the solvent from the first phase into the second, thus:

$$\nu_0 = -1,\ \nu_1 = 0,\ \nu_2 = 0,\ \ldots\ \nu'_0 = \frac{m_0}{m'_0}.$$

Hence, by (197), equilibrium requires that :

$$-\log\frac{n_0}{n} = \log\frac{n}{n_0} = \log K.$$

Now :

$$\frac{n}{n_0} = 1 + \frac{n_1 + n_2 + \ \dots}{n_0}$$

and therefore, since the fraction on the right is very small :

$$\frac{n_1 + n_2 + \ \dots}{n_0} = \log K \quad . \quad . \quad . \quad (209)$$

According to the general definition of (197) we here have :

$$\log K = \frac{1}{R}(\nu_0\phi_0 + \nu_1\phi_1 + \nu_2\phi_2 + \ \dots \ + \nu'_0\phi'_0).$$

Consequently, if we insert the values of the ν's, we get :

$$\frac{n_1 + n_2 + n_3 + \ \dots}{n_0} = \frac{1}{R}\left(\frac{m_0}{m'_0}\phi'_0 - \phi_0\right) = \log K \quad (210)$$

According to this equation $\log K$ is also very small.

If we compare this condition for equilibrium with the corresponding condition (202) which was established for the pure solvent, it is evident that the pressure of the dissolved moles n_1, n_2, n_3 . . . effects a deviation from the relationship between pressure and temperature that holds for the pure solvent; moreover, this deviation depends only on the total number of dissolved moles but not on their nature. To formulate this appropriately we can use either p or T as the independent variable. In the former case we say : at a definite pressure p the boiling or the freezing temperature T of the solution differs from that of the pure solvent. In the second case we say : for a definite temperature T the vapour pressure or the solidifaction pressure of the solution differs from that of the pure solvent. We proceed to calculate the deviations in each case.

If T_0 is the boiling or the freezing temperature of the pure solvent at the pressure p, we have by (202) :

$$(\log K)_{T_0} = 0$$

and, by subtracting (210):

$$(\log K)_T - (\log K)_{T_0} = \frac{n_1 + n_2 + \ . \ . \ .}{n_0}.$$

Now since T differs only slightly from T_0 we obtain by applying Taylor's Theorem and making use of (199):

$$\frac{\partial \log K}{\partial T}(T - T_0) = \frac{r}{RT^2}(T - T_0) = \frac{n_1 + n_2 + \ . \ . \ .}{n_0}.$$

From this it follows that:

$$T - T_0 = \frac{n_1 + n_2 + \ . \ . \ .}{n_0} \cdot \frac{RT^2}{r} \quad . \quad . \quad (211)$$

This is van't Hoff's law for the raising of the boiling point or the lowering of the freezing point, respectively. For in the case of solidification r, the heat transferred from outside to a liquid mole, is negative. Since n_0 and r occur multiplied together in the formula, it tells us nothing about the number of moles n_0 and the weight m_0 of a mole of the solvent. If r is expressed in calories we must, by (57), set $R = 1{\cdot}983$.

Thus for the vaporization of 1 litre of water at atmospheric pressure we have, very approximately, $n_0 r = 1000.539$ calories, $T = 373$. Hence the boiling point of a dilute aqueous solution becomes raised by the amount:

$$T - T_0 = 0{\cdot}51^\circ \, . \, (n_1 + n_2 + n_3 + \ . \ . \ .) \quad . \quad (212)$$

Further, when 1 litre of water freezes under atmospheric pressure, we have, very approximately, $n_0 r = - 1000.80$ calories, $T = 273$ and hence the boiling point of a dilute aqueous solution is:

$$T_0 - T' = 1{\cdot}85^\circ \, . \, (n_1 + n_2 + n_3 + \ . \ . \ .) \quad . \quad (213)$$

If on the other hand p_0 is the vapour pressure of the pure solvent at the temperature T', we have by (202):

$$(\log K)_{p_0} = 0$$

and by subtracting (210):

$$(\log K)_p - (\log K)_{p_0} = \frac{n_1 + n_2 + \ . \ . \ .}{n_0}.$$

Since p differs only slightly from p_0, we may, using (200), write :

$$\frac{\partial \log K}{\partial p}(p - p_0) = -\frac{v}{RT}(p - p_0) = \frac{n_1 + n_2 + \ . \ . \ .}{n_0}.$$

From this it follows, if we set v, the volume increase during the isothermal–isobaric vaporization of a liquid mole, equal to the volume of the resulting gaseous moles, $v = \frac{m_0}{m'_0}\frac{RT}{p}$, that :

$$\frac{p_0 - p}{p} = \frac{m'_0}{m_0} \cdot \frac{n_1 + n_2 + \ . \ . \ .}{n_0} \quad . \quad . \quad (214)$$

This is van't Hoff's law of the relative lowering of the vapour pressure. Since n_0 and m_0 occur only as a product, this formula tells us nothing of the weight of a mole of the liquid solvent.

Sometimes we find this relation expressed in the form that the relative lowering of the vapour pressure gives the ratio of the number of moles of the solvent n_0 to the number of moles n of the solution, or, what comes to the same thing in the case of dilute solutions, to the total number of moles of the solution. But, as we see here, this law holds only if $m'_0 = m_0$, that is, if the moles of the solvent in the solution and in the vapour are the same. Moreover, in general, this will not be so; as, for example, in the case of water.

The result is that each of the equilibrium states last treated, namely boiling point, freezing point, vapour pressure of a dilute solution, contains a method for determining the total number $n_1 + n_2 + \ . \ . \ .$ of foreign moles present in the solution. If the number thus found by measurement deviates from the number calculated from the percentage content of the solution on the assumption of normal moles, then by the theory above developed a chemical change of the moles by dissociation, association or such-like processes must necessarily have occurred. It is not possible, however, to deduce from the theory *what* type of change has occurred, that is, whether the dissociation, for example, was electrolytic or electrically neutral.

§ 78. **Both phases contain the two components in appreciable quantity.** If during the vaporization or freezing of a solution the solute vaporizes or freezes at the same time, the laws deduced in the previous section become modified in a way which we shall now investigate. The symbol for such a system is :

$$n_0 m_0,\ n_1 m_1,\ n_2 m_2,\ \ldots \ \big|\ n'_0 m'_0,\ n'_1 m'_1,\ n'_2 m'_2,\ \ldots$$

where, as hitherto, the index 0 refers to the solvent while the remaining indices refer to the different kinds of moles of the solute. If we perform exactly the same calculations as in the previous paragraph, we get instead of (120) the following equation :

$$\frac{n_1 + n_2 + \ldots}{n_0} - \frac{m_0}{m'_0} \cdot \frac{n'_1 + n'_2 + \ldots}{n'_0} = \log K \qquad (215)$$

and for the raising of the boiling point, instead of (211) :

$$T - T_0 = \left(\frac{n_1 + n_2 + \ldots}{n_0 m_0} - \frac{n'_1 + n'_2 + \ldots}{n'_0 m'_0}\right) \cdot \frac{m_0 R T^2}{r} \qquad (216)$$

Here r is the heat of transformation corresponding to the isothermal–isobaric vaporization of a mole of the solvent; so that $\frac{r}{m_0}$ is the heat of transformation for the vaporization of unit mass.

We again observe that in each of the two phases the mass of the solvent enters into the formula but not the number of moles or the molar weight, whereas in the case of the solute the number of moles exerts a characteristic influence on the boiling-point. Moreover the formula contains a generalization of van't Hoff's law, in that here we have, instead of the number of moles dissolved in the liquid $n_1 + n_2 + \ldots$, the difference in the number of moles dissolved in unit mass of the liquid and in unit mass of the vapour. According as unit mass of the liquid or unit mass of the vapour contains more dissolved moles, the boiling point of the solution is raised or lowered respectively. In the limiting case when both amounts are equal, that is the solution " boils constantly," the change in the boiling point is zero. Corresponding laws hold of course for the change of vapour pressure and the change of the freezing point. Corresponding to solutions with constant boiling points we have "eutectic amalgams" whose composition does not alter during the melting process. Such amalgams therefore have a melting point which is independent of the concentration.

PART TWO

THE CONDUCTION OF HEAT

CHAPTER I

FUNDAMENTAL EQUATION

§ 79. WHEREAS time entered in no way into the questions considered in the first part of this book, since we were concerned only with the direction and never with the rate of events that occurred in physical nature, we shall now turn our attention to the course of irreversible occurrences in time. For irreversible thermodynamic processes are only ideal and occur infinitely slowly (§ 25). We have now to deal with friction, including flow through a valve, heat conduction and diffusion. For all these processes laws hold which are to some extent analogous. We shall choose from among phenomena the simplest, heat conduction, and shall accordingly consider the time change of temperature at the different points of a non-uniformly heated, rigid, and homogeneous body at rest. As we wish to exclude all motions we shall also neglect the variations in density and volume caused by the changes in temperature.

Heat conduction in a body consists in the transport of energy effected by the interactions of the contiguous material elements of the body which are at different temperatures. Measurements in heat conduction consist in determining the temperature T as a function of the space-co-ordinates x, y, z and the time t. To be able to derive the fundamental law for calculating this function in a given case we must apply the two fundamental laws of thermodynamics. Let us consider the first law. This states that the amount of energy contained in any arbitrarily selected part of a body in the element of time dt changes according to the action exerted on this part of the body from without (§ 18). Now since the external actions in the present case are neither mechanical nor electromagnetic by nature but exclusively thermal their amount is simply the quantity of heat Q transferred during the time dt by conduction to the selected part of the body from without.

The transference of heat takes place through the surface of this part; it is thus composed of the sum of all the quantities of heat that pass into the interior through all the individual surface elements $d\sigma$ during the time dt. We therefore denote such a quantity of heat by $\mathfrak{q}_\nu \, d\sigma \, dt$, where ν stands for the inward direction of the normal to the part of the body in question, and we regard $\mathfrak{q}_\nu$ as a finite quantity. By applying the energy principle to an element of the body in the form of an infinitely small tetrahedron it may be proved, exactly as in III, § 4 for the flux of electromagnetic energy, that $\mathfrak{q}$ is a vector, the " vector of heat conduction," and the principle of the conservation of energy when applied to any arbitrarily selected part of the body states :

$$\frac{\partial E}{\partial t} dt = dt \int ck \frac{\partial T}{\partial t} \, . \, d\tau = dt \int \mathfrak{q}_\nu d\sigma \qquad . \quad (217)$$

where $d\tau$ denotes an element of volume, k the density, hence $kd\tau$ an element of mass, c the specific heat at constant volume, which we consider constant (§ 20).

If we transform the surface integral into a space integral by II (78):

$$\int (\mathfrak{q}_x \cos \nu x + \mathfrak{q}_y \cos \nu y + \mathfrak{q}_z \cos \nu z) d\sigma = - \int \operatorname{div} \mathfrak{q} \, . \, d\tau$$

then the equation (217) may be written in the form :

$$\int \left(ck \frac{\partial T}{\partial t} + \operatorname{div} \mathfrak{q} \right) d\tau = 0$$

and if we make the part of the body infinitely small, so that its volume shrinks to that of a single element $d\tau$, the expression for the first law becomes :

$$ck \frac{\partial T}{\partial t} + \operatorname{div} \mathfrak{q} = 0 \quad . \qquad . \qquad (218)$$

which holds for any place and time.

§ 80. To apply the *second* law of thermodynamics to any part of the body we choose the inequality of § 53 which holds generally for every irreversible process :

$$dS + dS_a > 0 \quad . \quad . \qquad . \quad . \qquad (219)$$

Here dS is the change of entropy of the part of the body or the sum of the entropy changes of all its mass elements $kd\tau$. Since volume changes do not come into consideration the change of entropy of a mass element $kd\tau$ is, by (82), equal to its change of energy divided by its temperature. So :

$$dS = \int \frac{1}{T} \,.\, ck \frac{\partial T}{\partial t} \,.\, d\tau \,.\, dt \qquad (220)$$

On the other hand dS_a is the change of entropy of the surrounding parts of the body. But since the entropy change of any body, as we saw in § 52 in the case of heat reservoirs, is equal to the quotient of the heat transferred from without by its temperature, the entropy change of that part of the surroundings which lies on the outer side of the surface element $d\sigma$ is :

$$-\frac{1}{T}\,q_\nu d\sigma dt.$$

For $qd\sigma dt$ is the amount of heat taken from this part in the time dt. This gives for the entropy change of the whole surroundings :

$$dS_a = -\,dt \int \frac{q_\nu}{T}\,\partial\sigma.$$

Substituting in (219) we get :

$$\int \frac{ck}{T}\frac{\partial T}{\partial t}\,d\tau - \int \frac{q_\nu}{T}\,d\sigma > 0$$

or, by transforming the surface integral into a space integral, as above, and applying the result to an infinitely small part of the body we get :

$$\frac{ck}{T}\frac{\partial T}{\partial t} + \operatorname{div}\left(\frac{q}{T}\right) > 0 \quad . \quad . \quad . \quad . \qquad (221)$$

as the expression of the second law, which holds for any place and time.

If we expand the expression for the divergence :

$$\operatorname{div}\left(\frac{q}{T}\right) = \frac{\partial \frac{q_x}{T}}{\partial x} + \frac{\partial \frac{q_y}{T}}{\partial y} + \frac{\partial \frac{q_z}{T}}{\partial z}$$

$$= \frac{1}{T}\operatorname{div} q - \frac{1}{T^2}(q \,.\, \operatorname{grad} T),$$

substitute this in (221) and make use of equation (218) of the first law, we see that the second law requires that :

$$q \,.\, \operatorname{grad} T < 0 \quad . \quad . \quad . \quad . \quad (222)$$

More than this cannot be deduced from the second law.

An analogous equation can be set up for any other irreversible process, for example, for diffusion.

§ 81. To arrive at a differential equation for heat conduction it is necessary to make a plausible physical assumption which will allow us to introduce a quantitative relationship between the vectors q and grad T, which will replace the inequality (222) by a precise equation. For isotropic substances, to which we shall restrict our attention in the sequel, such an assumption suggests itself immediately. For since no favoured directions exist in an isotropic substance, nothing remains but to set the two vectors q and grad T proportional to each other, thus :

$$q = -\kappa \operatorname{grad} T \quad . \quad . \quad . \quad (223)$$

which identically satisfies the inequality (222), if the constant κ, the so-called coefficient of heat conductivity of the substance, is taken as positive.

Substituting this value of q in the equation (218) of the first law we get as the fundamental equation of heat conduction :

$$\frac{\partial T}{\partial t} = a^2 \,.\, \Delta T,$$

where we have written a^2 for the positive constant $\frac{\kappa}{ck}$, that is :

$$\frac{\kappa}{ck} = a^2 \quad . \quad . \quad . \quad . \qquad (224)$$

Since for mathematical reasons it is often convenient to calculate with a zero point of temperature, whereas on the other hand the zero point of the absolute temperature T is not attainable physically, it is found advantageous in dealing with problems of heat conduction to use instead of the absolute temperature T the temperature θ referred to the freezing point of water and defined by (95), so that the differential equation for heat conduction becomes :

$$\frac{\partial \theta}{\partial t} = a^2 \Delta \theta \quad . \quad . \quad . \quad . \quad . \quad . \qquad (225)$$

To some extent it resembles in form the wave-equation II (222). But there is the fundamental difference that in the wave-equation the second differential coefficient with respect to the time occurs, whereas here it is the first differential coefficient. This corresponds with the irreversibility of the process of heat conduction, which excludes the possibility of reversing the time, whereas this is possible in the case of vibration phenomena. It is also connected with this circumstance that the constant a, which signifies a velocity in the wave-equation, has in the case of heat conduction the dimensions of length divided by the square root of the time.

CHAPTER II

INTERNAL HEAT CONDUCTION

§ 82. We shall apply the term *internal* conduction of heat to those problems in which the temperature at the whole surface of the body in question is given for all times. Our task is then to integrate (225) for prescribed boundary values of θ. We shall first convince ourselves that if in addition the initial temperature at all points of the body is also known, only one solution of the problem exists. For, if there were two solutions, θ and θ', the difference $\theta' - \theta = \theta_0$ would represent a function of space and time which would likewise satisfy the differential equation (225), and would moreover vanish for $t = 0$ at all points, and at the surface it would vanish at *all* times.

Let us now consider the positive integral (cf. II (81)) taken over the whole body :

$$J = \int d\tau \left\{ \left(\frac{\partial\theta_0}{\partial x}\right)^2 + \left(\frac{\partial\theta_0}{\partial y}\right)^2 + \left(\frac{\partial\theta_0}{\partial z}\right)^2 \right\}$$
$$= -\int d\sigma \theta_0 \frac{\partial\theta_0}{\partial\nu} - \int d\tau \theta_0 \Delta\theta_0.$$

Here the surface integral vanishes, since θ_0 is zero everywhere on the surface; and from (225) we get :

$$J = -\frac{1}{a^2}\int \theta_0 \frac{\partial\theta_0}{\partial t} d\tau = -\frac{1}{2a^2}\frac{\partial}{\partial t}\int \theta_0{}^2 d\tau \quad . \quad . \quad (226)$$

Since J is positive it follows that the positive integral $\int\theta_0{}^2 d\tau$ can only decrease as the time t increases. But this integral vanishes for $t = 0$. Hence it continually remains zero and therefore θ_0 also vanishes at all places and for all times, so that the solutions θ' and θ become identical.

We can draw a further general conclusion from this result. If θ is given as before at the surface for all times, so that $\theta' - \theta = \theta_0$ vanishes there at all times, whereas we now assume that the initial state, and so also the function θ_0, are arbitrary for $t = 0$, we can deduce from (226) that the integral $\int \theta_0^2 d\tau$ which may have any finite values initially, when $t = 0$, continually decreases in the course of time, and so the quantity θ_0 and consequently also the difference of the two solutions θ and θ' continually decrease until they finally vanish. This may be interpreted physically as follows. If the temperature over the whole of the surface of the body is given as a function of the time, then the temperature in the interior, whatever its initial value may have been, also gradually approaches a perfectly definite time function which is independent of the original distribution of temperature. This is also an expression of the irreversible character of heat conduction.

We shall now fix our attention on several simple particular solutions of the problem which are of physical interest.

§ 83. Let us first take the stationary states, that is, those states for which the temperature at any place is independent of the time. For then we have, by (225), the condition :

$$\Delta\theta = 0 \quad . \quad . \quad . \quad (227)$$

If the temperature given for the surface is everywhere constant in time, then, as we have seen, a perfectly definite state establishes itself in the interior in the course of time, no matter what the initial temperature may have been. By III, § 19 we see that θ, in fact, is uniquely defined by (227) and the boundary condition.

If θ depends only on a single co-ordinate, say x, (227) reduces to :

$$\frac{\partial^2\theta}{\partial x^2} = 0$$

and we obtain the law for stationary linear heat conduction :

$$\frac{\partial \theta}{\partial x} = \text{const. or } q_x = \text{const.}$$

for which the temperature gradient and with it the heat current have constant magnitude and direction. Their amounts are determined by the value of the temperature θ at two different points x, corresponding exactly with the properties of the electric potential in a homogeneous electric field (III, § 16).

§ 84. We shall now assume that θ depends on the time t as well as on x. Equation (225) then runs :

$$\frac{\partial \theta}{\partial t} = a^2 \frac{\partial^2 \theta}{\partial x^2} \quad . \quad . \qquad (228)$$

A simple particular solution is obtained by setting :

$$\theta = e^{\alpha t + \beta x} \quad . \quad . \quad . \quad . \quad . \qquad (229)$$

Then (228) is satisfied by the relation :

$$\alpha = a^2 \beta^2.$$

Particular interest attaches to those events in which the temperature varies periodically with the time. Hence we take α as purely imaginary :

$$\alpha = \omega i$$

and then obtain :

$$\beta = \frac{\sqrt{\alpha}}{a} = \pm \frac{\sqrt{\omega}}{a} \cdot \frac{1 + i}{\sqrt{2}} .$$

We choose the lower sign here in order that θ may not become infinitely great for $x = + \infty$. By substituting this value for β in (229) and omitting the imaginary part we obtain as the solution of the differential equation (228) :

$$\theta = e^{-\sqrt{\frac{\omega}{2}} \frac{x}{a}} \cos \left(\omega t - \sqrt{\frac{\omega}{2}} \frac{x}{a} \right)$$

or, a little more generally, if θ_0 and θ_1 denote any two constants :

$$\theta = \theta_1 e^{-\sqrt{\frac{\omega}{2}} \frac{x}{a}} \cos \left(\omega t - \sqrt{\frac{\omega}{2}} \frac{x}{a} \right) + \theta_0 \quad . \quad . \qquad (230)$$

If we suppose the body to reach from $x = 0$ to $x = +\infty$ the expression (230) represents an event which, independently of the initial state, takes place in the interior of the body in the course of time if the temperature at the bounding surface $x = 0$ varies with a single period given by:

$$\theta = \theta_1 \cos \omega t + \theta_0 \quad . \quad . \quad . \quad . \quad (231)$$

The amplitude of the vibration is θ_1, the mean temperature θ_0, the period of vibration $\tau = \frac{2\pi}{\omega}$.

By (230) the process may be pictured as occurring in the following way: heat waves from the bounding surface $x = 0$ penetrate into the body; these waves are conditioned by the temperature-vibration at the boundary and their amplitude decreases more or less rapidly as the distance x from the bounding surface increases. The wave-length is:

$$\lambda = 2\pi a \sqrt{\frac{2}{\omega}} = 2a\sqrt{\pi\tau} \qquad (232)$$

The velocity of propagation is:

$$u = \omega \,.\, a\sqrt{\frac{2}{\omega}} = 2a\sqrt{\frac{\pi}{\tau}} \quad . \quad . \quad (233)$$

The constant of space damping is:

$$\frac{1}{a}\sqrt{\frac{\omega}{2}} = \frac{1}{a}\sqrt{\frac{\pi}{\tau}} \quad . \quad . \qquad (234)$$

Thus the more rapidly the vibrations occur the shorter the waves become, the more rapidly they propagate themselves in the body and the less deeply they penetrate into it.

A simple example of such periodic vibrations is given to a certain degree of approximation by the temperature fluctuations at the surface of the earth. In this case two different periods can be distinguished, the diurnal and the annual period. Corresponding to them there are two different kinds of heat waves that penetrate into the body of the earth. The first are shorter than the second and although they propagate themselves more rapidly, they penetrate less deeply than the second. These deductions from the theory have been satisfactorily confirmed by measurements. The velocity of propagation amounts to about 1 metre per day for the waves of the diurnal period and about 0·046 metre per day for the annual period. Since the constant a is the same in both cases the ratio of these two numbers should, by (233), be equal to the square root of the number of days in a year, that is, to $\sqrt{365}$, which is a sufficiently good agreement, if we consider that the actual temperature fluctuations are not singly periodic and that the earth is not a homogeneous body.

Exactly as for singly periodic fluctuations of temperatures at the surface $x=0$ the problem may be solved for any arbitrarily prescribed temperature fluctuations by resolving the given time function into a Fourier series (II, § 38) and superposing the corresponding solutions (230).

§ 85. Another method of finding a particular solution of the differential equation (228) is based on the introduction of new independent variables. Instead of t and x we shall now introduce the independent variables t and $u=\frac{x}{\sqrt{t}}$ where we always take the positive sign for the root. This substitution suggests itself to some extent because u has the dimensions of the constant a of heat conduction. We then have:

$$\left(\frac{\partial\theta}{\partial t}\right)_x=\left(\frac{\partial\theta}{\partial t}\right)_u+\left(\frac{\partial\theta}{\partial u}\right)_t\cdot\left(\frac{\partial u}{\partial t}\right)_x=\left(\frac{\partial\theta}{\partial t}\right)_u-\frac{1}{2}\frac{x}{\sqrt{t^3}}\left(\frac{\partial\theta}{\partial u}\right)_t$$

$$=\left(\frac{\partial\theta}{\partial t}\right)_u-\frac{1}{2}\frac{u}{t}\left(\frac{\partial\theta}{\partial u}\right)_t.$$

Further:

$$\left(\frac{\partial\theta}{\partial x}\right)_t=\left(\frac{\partial\theta}{\partial u}\right)_t\cdot\left(\frac{\partial u}{\partial x}\right)_t=\frac{1}{\sqrt{t}}\left(\frac{\partial\theta}{\partial u}\right)_t$$

and:

$$\left(\frac{\partial^2\theta}{\partial x^2}\right)_t=\frac{1}{t}\left(\frac{\partial^2\theta}{\partial u^2}\right)_t$$

and hence by substituting in (228):

$$\frac{\partial\theta}{\partial t}-\frac{1}{2}\frac{u\partial\theta}{t\partial u}=\frac{a^2}{t}\frac{\partial^2\theta}{\partial u^2}$$

or:

$$a^2\frac{\partial^2\theta}{\partial u^2}+\frac{u}{2}\frac{\partial\theta}{\partial u}=t\,.\,\frac{\partial\theta}{\partial t}.$$

This differential equation is satisfied by setting $\frac{\partial\theta}{\partial t}=0$ and also:

$$a^2\frac{\partial^2\theta}{\partial u^2}+\frac{u}{2}\frac{\partial\theta}{\partial u}=0$$

which may be written in the form:

$$\frac{d\left(\frac{d\theta}{du}\right)}{\frac{d\theta}{du}}=-\frac{udu}{2a^2}$$

or:

$$\log\frac{d\theta}{du}=-\frac{u^2}{4a^2}+\text{const.}$$

$$\frac{d\theta}{du}=C'\,.\,e^{-\frac{u^2}{4a^2}}$$

$$\theta=C\,.\int^u e^{-\frac{u^2}{4a^2}}du.$$

Let us first consider the special case in which $\theta=0$ for $u=0$ and $\theta=1$ for $u=+\infty$. The lower limit of the integral then becomes zero, and the constant C becomes equal to the reciprocal value of Laplace's integral (IV, § 47):

$$\int_0^\infty e^{-\frac{u^2}{4a^2}}du=\frac{1}{2}\cdot 2a\sqrt{\pi}=a\sqrt{\pi}$$

and hence:

$$\theta=\frac{1}{a\sqrt{\pi}}\cdot\int_0^u e^{-\frac{u^2}{4a^2}}du.$$

To simplify this expression we shall introduce in place of the integration variable $u = \frac{x}{\sqrt{t}}$ the variable :

$$\xi = \frac{u}{2a}$$

and so obtain as a particular integral of the equation of heat conduction (228) :

$$\theta = \frac{2}{\sqrt{\pi}} \cdot \int_0^{\frac{x}{2a\sqrt{t}}} e^{-\xi^2}\, d\xi \quad . \quad . \quad . \qquad (235)$$

Let us consider its physical significance for the case where the body extends from $x = -\infty$ to $x = +\infty$ and the process occurs from the time $t = 0$ till $t = \infty$. Initially, when $t = 0$, we have $\theta = -1$ for all points on the negative side, $\theta = 1$ for all points on the positive side, whereas $\theta = 0$ and remains at that value for $x = 0$. As t increases the temperature on the positive side gradually falls to zero, the more slowly the further the point is situated from the origin; whereas on the negative side the temperature increases in an exactly analogous way towards the zero value. Finally, when $t = \infty$ the temperature has become zero for all finite values of x.

This course of events may be considered to be realized by the following process. Bring into contact two very large bodies of the same material, one of which is at the temperature of 1° C., the other at the temperature of − 1° C., in such a way that their plane boundary surfaces ($x = 0$) touch. Now consider the way in which the temperatures balance. Since the initial state and the boundary conditions correspond to the expression (235) and since only a single solution of the problem exists the process must occur in the manner prescribed by (235).

From this we see, among other things, according to what law the cooling in the originally warmer body takes place. As the time t increases the cooling advances continually further into the interior. But nevertheless there is no sense in talking of a certain velocity of propagation of a heat wave or a cooling wave; for, no matter how small the time t may be, the temperature change at any distance however great already has a finite value. The characteristic feature of the process is rather the fact that the temperature at every point x depends only on the one quantity $\frac{x}{\sqrt{t}}$, so that for every place the time has a definite order of magnitude within which the temperature change becomes appreciable; the nearer the boundary surface is the sooner this time arrives.

The behaviour of the temperature near the boundary surface $x = 0$ is of special interest. In general the temperature gradient is, by (235):

$$\frac{\partial \theta}{\partial x} = \frac{1}{a\sqrt{\pi t}} \cdot e^{-\frac{x^2}{4a^2 t}} \quad . \quad . \quad (236)$$

and for $x = 0$:

$$\left(\frac{\partial \theta}{\partial x}\right)_{x=0} = \frac{1}{a\sqrt{\pi t}} \quad . \quad . \quad . \quad (237)$$

By (223) the temperature gradient at the same time gives us the amount of the heat conducted from the one body into the other. For $t = 0$ this amount is infinitely great and then decreases, at first rapidly and then progressively more slowly until it becomes vanishingly small. It is noteworthy too that the question of the value of θ for $x = 0$ and $t = 0$ admits of no definite answer. For this answer depends on the way in which the two independent variables change in crossing the boundary. According as x or $\sqrt{t}$ is of the higher order of magnitude, $\theta = 1$ or 0, and when they are of the same order of magnitude θ has some value between 1 and 0.

The particular solution (235) of the equation of heat conduction may be directly generalized into the following form:

$$\theta = \frac{2A}{\sqrt{\pi}} \cdot \int_0^{\frac{x}{2a\sqrt{t}}} e^{-\xi^2}\, d\xi + B \quad . \quad . \quad (238)$$

where A and B denote two arbitrary constants. This solution can be adapted to the case where one of the two bodies ($x > 0$) is initially at the temperature θ_1, while the other ($x < 0$) is initially at the temperature θ_2. Then when $t = 0$ we have for the first, by (238), that $\theta_1 = A + B$ and for the second that $\theta_2 = -A + B$; this gives us the value of the two constants:

$$A = \frac{\theta_1 - \theta_2}{2},\ B = \frac{\theta_1 + \theta_2}{2} \quad . \quad . \quad . \quad (239)$$

When the body in question does not extend to infinity in both directions but is bounded by the plane $x = 0$ on the one side and reaches to $x = +\infty$ on the other side, (238) represents the change of the temperature for the case where the initial temperature is uniform and of the value $A + B$ and the surface of the body, $x = 0$, is kept constantly at the temperature B.

§ 86. An interesting application of the last formula was made by Sir William Thomson (Lord Kelvin) in connexion with the question of the age of the earth. If we consider the earth as homogeneous and infinite in extent and having the plane surface $x = 0$ as its boundary, and if we take the time $t = 0$ from the instant when the solidification of the earth, supposed liquid previously, had advanced from the interior to the surface, that is, it is everywhere at the temperature at which molten masses of rock solidify, say 4000° C., then we obtain from (238) the law for the secular cooling of the earth, if we assume that from the very beginning the temperature of the surface was constant, say $\theta = 0°$ C. For then, by the last remark of § 85 we must set $B = 0$, $A = 4000$ and then (238) gives us the value of the temperature θ for every place and time.

In particular the temperature gradient or the flow of heat by conduction, respectively, is determined at the surface, if we generalize (237), by:

$$\left(\frac{\partial \theta}{\partial x}\right)_{x=0} = \frac{A}{a\sqrt{\pi t}} \quad . \quad . \quad (240)$$

Actual measurements show an increase of temperature by 1° as the depth increases by about 25 metres. Hence for the present time we have :

$$\frac{A}{a\sqrt{\pi t}} = \frac{1}{25} \text{ degree per metre.}$$

Now in § 84 we found that the velocity of propagation (233) of the diurnal period of the temperature for τ, which equals one day, is equal to one metre, that is, $2a\sqrt{\pi} = 1$.

Substituted in the last equation this gives :

$$\frac{2A}{\sqrt{t}} = \frac{1}{25}$$

and for the value $A = 4000$ this becomes :

$t = 4.10^{10}$ days, that is, about 100 million years

for the age of the earth, calculated from the time at which its crust solidified. This estimate is in reality far too low, which is clearly due to the inadequate assumptions made. We shall find occasion to improve on one of them later (§ 89).

§ 87. Another generalization of the particular solution (235), which is of still more far reaching importance, can be obtained if we first start out from the simple solution θ of the equation of heat conduction (228), which is obtained by differentiating (235) with respect to x :

$$\theta = \frac{1}{a\sqrt{\pi t}} \cdot e^{-\frac{x^2}{4a^2t}} \quad . \tag{241}$$

Regarded physically, this is the temperature in a body which extends from $x = -\infty$ to $x = +\infty$ and in which initially, when $t = 0$, the temperature is everywhere zero except at the plane $x = 0$, where it is infinitely great. As t increases the heat flows away to both sides, so that at $t = \infty$ the temperature becomes zero everywhere.

This particular solution may now be generalized by displacing the favoured plane from the position $x = 0$ to any other position $x = \xi$ and by adding together an infinite number of such solutions with an infinite number of favoured points ξ lying very close to one another at a distance $d\xi$, each solution having been multiplied by any infinitely small constant peculiar to the point ξ, thus $f(\xi) \,.\, d\xi$. We then get as the solution of the equation of heat conduction (228):

$$\theta = \frac{1}{a\sqrt{\pi t}}\int_{-\infty}^{+\infty} e^{-\frac{(x-\xi)^2}{4a^2t}} \,.\, f(\xi)\,.\,d\xi \quad . \quad . \quad (242)$$

Closer inspection shows that this is the general solution. For by choosing $f(\xi)$ suitably this solution can be adapted to any arbitrary initial state. To take an actual case: at the time $t = 0$ let the temperature $\theta_0(x)$ be given in some way for all values of x between $-\infty$ and $+\infty$. Let us on the other hand now calculate the temperature θ from (242) for $t = 0$. If we first take t as very small, the integrand in (242) vanishes for all values of ξ except those which lie very near the value x. Hence if we introduce $\xi - x = \epsilon$ in place of ξ as the variable of integration, the integral in (242) reduces to:

$$\int_{-\varepsilon_1}^{+\varepsilon_1} e^{-\frac{\varepsilon^2}{4a^2t}} \,.\, f(x+\epsilon)\,.\,d\epsilon$$

where ϵ_1, the limiting value of ϵ, is small compared with x, but large compared with $a\sqrt{t}$. Or, if we make the substitution $\eta = \dfrac{\epsilon}{2a\sqrt{t}}$ and omit ϵ in the argument of the function f:

$$2a\sqrt{t}\,.\,f(x)\int_{-\infty}^{+\infty} e^{-\eta^2}\,d\eta = 2a\sqrt{\pi t}\,.\,f(x).$$

If this value of the integral is substituted in (242) we get for $t = 0$:

$$\theta_0 = 2f(x)$$

which relates $f(x)$ to θ_0. In this way we obtain the temperature of the body at any point x for any time t, if the temperature $\theta_0(x)$ is given in some way for $t = 0$ for all points from $x = -\infty$ to $x = +\infty$:

$$\theta = \frac{1}{2a\sqrt{\pi t}}\int_{-\infty}^{+\infty} e^{-\frac{(\xi-x)^2}{4a^2t}} \,.\, \theta_0(\xi)\,.\,d\xi \quad . \quad (243)$$

This general solution of course contains the particular solution (235) previously obtained for a special case. For if we set $\theta_0(\xi) = -1$ for $\xi < 0$, $\theta_0(\xi) = +1$ for $\xi > 0$, then (243) becomes transformed into (235), as may easily be verified by calculation.

§ 88. We shall here add the case where the two homogeneous bodies which are in contact along the plane $x = 0$ and extend to infinity on opposite sides, have the initial temperatures θ_1 and θ_2 but do not consist of the same substance; that is, their constants a and a' of heat conduction are different. The solution of the problem is then also obtained from the expression (238) by inserting the constants a, A, B for positive values of x and the constants a', A', B' for negative values of x. While a and a' are given at the beginning we have also four equations to determine the four quantities A, B, A', B'. Two of these are the equations for the initial temperatures:

$$\theta_1 = A + B, \ \theta_2 = -A' + B'.$$

The third is the condition for a steady temperature at $x = 0$, $B = B'$. The fourth is the condition, which follows from the energy principle (cf. III, § 6), that the normal component $\mathfrak{q}_\nu$ of the heat current is constant: $\mathfrak{q}_\nu + \mathfrak{q}'_{\nu'} = 0$. Or, by (240):

$$\frac{A}{a} = \frac{A'}{a'},$$

so that everything is determined.

The preceding problem is to be included in those dealing with internal heat conduction because, on account of the assured constancy of the temperature, no other material constants occur apart from the conductivity (*Wärmeleitungskoeffizient*), κ or, respectively, the constant a of every body.

CHAPTER III

EXTERNAL HEAT CONDUCTION

§ 89. In reality the temperature at the common bounding surface of two bodies that are not in heat equilibrium is never constant, but always exhibits a more or less abrupt transition. In place of the condition for the constancy of the temperature another boundary condition then appears, which expresses a definite relation between the abrupt change of temperature (*Temperatursprung*) and the normal component of the heat current. The simplest relation is that in which we set the two quantities proportional to each other, thus:

$$q_\nu = h(\theta' - \theta) \quad . \quad . \quad . \quad . \quad . \qquad (244)$$

where ν denotes the inward normal of the body which has the temperature θ. The positive constant h is called the "coefficient of external heat conduction" or "external conductivity" and depends on the nature of both bodies. An infinitely great value of h denotes constant temperature, that is, the case treated in the preceding chapter; an infinitely small value of h, on the other hand, denotes thermal isolation, that is, it represents the adiabatic condition.

In discussing particular solutions we shall first link up with the problem of the secular cooling of the earth which was treated in § 86. We again assume the earth to extend from $x = 0$ to $x = \infty$ and to have an initial temperature of 4000° C. In § 86 we used as the boundary condition the equation $\theta = 0$ for $x = 0$ and any values of t, and we obtained as the solution the expression (238) with $B = 0$.

We now allow the temperature to undergo an abrupt transition at the bounding surface between the earth and external space, namely from θ to zero, and, by (244), we write for the heat current :

$$q_x = -\kappa\frac{\partial\theta}{\partial x} = -h\theta$$

or, if we set :

$$\frac{h}{\kappa} = b \qquad . \qquad . \quad . \quad (245)$$

we have :

$$\frac{\partial\theta}{\partial x} = b\theta \qquad . \qquad . \quad (246)$$

which holds for $x = 0$ and for all values of the time t. This formulates the problem completely. For $b = \infty$ the boundary condition becomes $\theta = 0$ and then the earlier solution (238) results.

For a finite value of b the solution can be obtained if we can determine the following function ϕ of x and t :

$$\theta - \frac{1}{b}\frac{\partial\theta}{\partial x} = \phi \quad . \qquad . \qquad . \quad (247)$$

This function ϕ satisfies the differential equation (228) in particular, if we insert ϕ in it instead of θ. Further $\phi = A$ when $t = 0$ since $\theta = A$ and $\frac{\partial\theta}{\partial x} = 0$. Lastly, on account of (246) $\phi = 0$ for $x = 0$ and for all values of t. From this it follows that the function ϕ is no other than that temperature which in § 86 represented the solution of the problem and which corresponds to an infinitely great value of b. So by (238) :

$$\phi = \frac{2A}{\sqrt{\pi}} \cdot \int_0^{\frac{x}{2a\sqrt{t}}} e^{-\xi^2} d\xi \qquad . \quad . \quad (248)$$

All that now remains is to calculate the function θ from the differential equation (247). This is a non-homogeneous linear equation of the first order in a single variable x. We integrate it by setting :

$$\theta = \psi \, . \, e^{bx} \quad . \qquad . \quad (249)$$

It then follows from (247) that :

$$-\frac{1}{b}\frac{\partial\psi}{\partial x}e^{bx} = \phi$$

and by integrating :

$$\psi = -b\int^{x} e^{-bx}\phi dx.$$

Hence, by (249) :

$$\theta = -b\,.\,e^{bx}\int_{\infty}^{x} e^{-bx}\phi dx \tag{250}$$

We must take ∞ for the lower limit of the integral, as otherwise θ would become infinitely great for $x = \infty$. The expression (250) for θ, together with the value (248) for ϕ, represents the solution of the problem. For $t = 0$ we have by (248) that $\phi = A$ and by (250) $\theta = A$, corresponding to the initial temperature; but at the surface $x = 0$, θ is not zero right from the beginning but changes continuously with the time t.

To be able to introduce ϕ in a somewhat less complicated way we first transform (250) by integrating by parts :

$$\theta = \phi - e^{bx}\int_{\infty}^{x} e^{-bx}\frac{\partial\phi}{\partial x}dx$$

and have now only to deal with $\frac{\partial\phi}{\partial x}$ in the integrand, that is, with an exponential function.

Since we are interested in the temperature at the surface of the earth we set $x = 0$ and obtain :

$$\theta = \int_{0}^{\infty} e^{-bx}\frac{\partial\phi}{\partial x}dx$$

or, substituting for ϕ from (248) :

$$\theta = \frac{A}{a\sqrt{\pi t}}\cdot\int_{0}^{\infty} e^{-\frac{x^2}{4a^2t}-bx}\,.\,dx\ .\quad .\quad . \tag{251}$$

This time-function represents the course of the temperature at the earth's surface. For small values of t the first term in the exponential predominates; θ then becomes equal to A. For large values of t the second term predominates; the integral then becomes equal to $\frac{1}{b}$ and:

$$\theta = \frac{A}{ab\sqrt{\pi t}} \quad . \qquad . \qquad (252)$$

If, as in § 86, we again wish to know the temperature gradient at the earth's surface, its value can be obtained directly from the boundary condition (246) as $b\theta$, and so for great values of t by (252):

$$\left(\frac{\partial \theta}{\partial x}\right)_{x=0} = \frac{A}{a\sqrt{\pi t}}$$

which is identical with (240). From this we see that by introducing a finite value for the external heat conduction the value of the temperature gradient at the earth's surface is not influenced at all for great values of t. External heat conduction thus seems to offer no prospects of accounting for the above-mentioned deviation of the age of the earth according to Thomson's theory from its actual age, which is much greater. The true reason is in fact to be sought in quite another quarter, namely the continual development of heat by radio-active processes which strongly counteract the cooling of the earth.

§ 90. Hitherto we have always imagined the body to extend to infinity. We shall now consider the case of a plane parallel plate of finite thickness with the boundary surfaces $x = 0$ and $x = l$, whose temperature θ at $t = 0$ we shall suppose given as an arbitrary function of the space co-ordinates. And we shall suppose that the body can exchange heat through its two boundary surfaces with the surrounding medium (air), which is at zero temperature, according to the law (246) of external heat conduction. We then require to integrate the differential equation (228) for θ, taking into account the boundary conditions:

$$\frac{\partial \theta}{\partial x} = b\theta. \qquad . \qquad (253)$$

for $x = 0$, and :

$$\frac{\partial\theta}{\partial x} = -b\theta \ . \qquad (254)$$

for $x = l$.

We treat this problem as in all similar cases by first finding a simple particular solution of the differential equation, which satisfies the boundary conditions. We then add together a sufficient number of such particular solutions, multiplied by appropriate constants, thus generalizing the solution in such a way that it can be adapted to the given initial state.

Let us apply this method first to the special case for which the constant b of external heat conduction becomes infinitely great. The two boundary conditions then reduce to $\theta = 0$ and the following expression offers itself as the simplest particular integral of (228) which also satisfies both boundary conditions :

$$\theta = \sin\frac{n\pi x}{l} \cdot e^{\gamma \cdot t} . \quad . \quad . \quad . \qquad (255)$$

where n denotes any integer. We see that the differential equation (228) is actually satisfied by setting :

$$\gamma = -\frac{a^2\pi^2n^2}{l^2} . \quad . \quad . \quad . \quad . \qquad (256)$$

and θ vanishes for both $x = 0$ and $x = l$.

In the initial state ($t = 0$) the spatial distribution of temperature in the case of the particular solution (255) is represented by a sine curve. But if we multiply the expression by a constant A_n and sum up over all values of n from 1 to ∞ (negative values of n do not add to the generalization), we obtain the general solution of the problem :

$$\theta = \sum_{n=1}^{n=\infty} A_n \, e^{\gamma_n t} \sin\frac{n\pi x}{l} \ . \quad . \qquad (257)$$

where the expression (256) is to be substituted for γ_n.

Actually the coefficients A_n can always be chosen in such a way that for $t = 0$ the temperature θ becomes any arbitrarily prescribed space function $\theta_0(x)$. For when $t = 0$ we obtain from (257):

$$\theta_0 = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{l} \quad . \quad . \quad . \quad . \quad . \qquad (258)$$

and this is a Fourier series (II (182)) with a period $x = 2l$, whose coefficients are uniquely determined if the function $\theta_0(x)$ is given in any way within the half period l (II, § 39).

§ 91. Reverting to our treatment of the general case in which the constant b of external heat conduction is finite we choose as the particular integral, generalizing (255):

$$\theta = \cos(\alpha x + \beta) \,.\, e^{\gamma t} \quad . \quad . \quad . \quad . \qquad (259)$$

The differential equation (228) is satisfied if we set:

$$\gamma = -a^2\alpha^2 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (260)$$

The first boundary condition (253) is satisfied if we set:

$$\tan\beta = -\frac{b}{\alpha} \quad . \quad . \quad . \quad . \quad . \qquad (261)$$

With these values for γ and β, and simplifying the expression (259) by dividing by $\cos\beta$, we get:

$$\theta = \left(\cos\alpha x + \frac{b}{\alpha}\sin\alpha x\right) . \, e^{-a^2\alpha^2 t} \quad . \qquad (262)$$

Here only the constant α, the "wave number" $\left(=\frac{2\pi}{\lambda}\right)$ is still arbitrary. We shall use it to satisfy the second boundary condition (254) as well. This gives, by (262):

$$\tan\alpha l = \frac{2\alpha b}{\alpha^2 - b^2} \quad . \quad . \qquad (263)$$

This equation which involves a transcendental function in α may be reduced to two simpler equations. For if we consider that on the one hand:

$$\tan\alpha l = \frac{2\tan\frac{\alpha l}{2}}{1 - \tan^2\frac{\alpha l}{2}}$$

and on the other hand :

$$\frac{2\alpha b}{\alpha^2 - b^2} = \frac{2\frac{b}{\alpha}}{1-\left(\frac{b}{\alpha}\right)^2} = \frac{-2\frac{\alpha}{b}}{1-\left(-\frac{\alpha}{b}\right)^2}$$

it follows that the equation (263) is satisfied by :

$$\tan\frac{\alpha l}{2} = \frac{b}{\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (264)$$

as well as by :

$$\tan\frac{\alpha l}{2} = -\frac{\alpha}{b} \quad . \quad . \quad . \qquad (265)$$

The roots of both equations can be clearly demonstrated by means of graphical representation if we plot the values of α, say, as the abscissæ and then look for the points of intersection of the curve $y = \tan\frac{\alpha l}{2}$ with one of the two curves $y = \frac{b}{\alpha}$ and $y = -\frac{\alpha}{b}$ (Fig. 6). The first curve is a tangent curve with the values 0 and ∞ succeeding each other regularly at distances $\frac{\pi}{l}$ apart. The second curve is an equilateral hyperbola with its branches in the first and the third quadrants, the co-ordinate axes being asymptotes. The third curve is a straight line which passes through the origin 0 and the second and fourth quadrants. In Fig. 6 only the positive α-axis is shown, as a reversal of the sign of α leads to nothing new.

We see from the figure that there are an infinite number of roots both on the hyperbola and on the straight line. If we number them in the order of their magnitude we obtain on the hyperbola the roots with odd indices : 1, 3, 5 . . . , and on the straight line those with even indices : 2, 4, 6 . . . A root $\alpha_0 = 0$ does not enter into the question, as we see from (262) if we set $\alpha = 0$ in it.

The quantities $\alpha_1, \alpha_2 \ldots \alpha_n \ldots$ which are determined by the equation (263) are called the "proper values" of the wave-number α, and the expressions (262) which involve the proper values of α are called the "proper functions" of the system in question. Even if the exact values of α_n cannot be directly given their approximate values can easily be read off from Fig. 6. Each of the

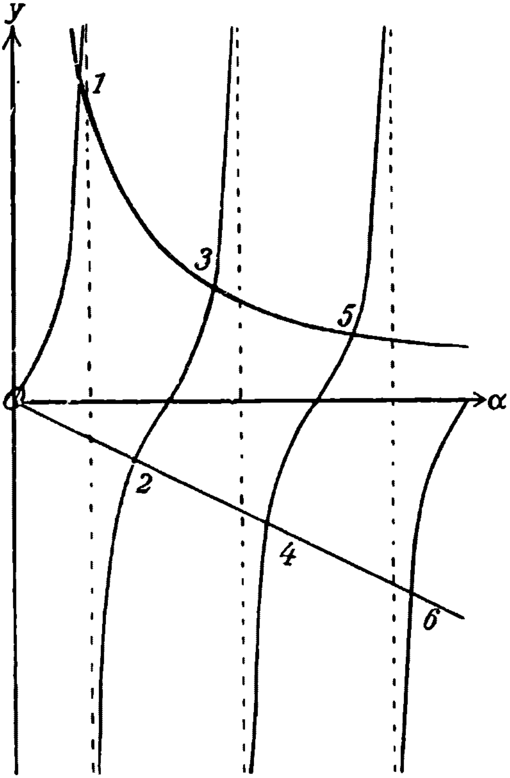

Fig. 6.

intervals marked off along the α-axis and of width $\frac{\pi}{l}$ evidently contains a root, so that:

$$(n-1)\frac{\pi}{l} < \alpha_n < \frac{n\pi}{l}.$$

As the order number n increases α_n approaches more and more closely to the lower limiting value $\frac{(n-1)\pi}{l}$ which for odd values of n (points of intersection with the hyperbola) denote the zero points of the curve of tangents, whereas the even values of n (points of intersection with the straight line) denote the points at infinity on the curve of tangents; so that the distance between two successive proper values α_n asymptotically approaches the value $\frac{\pi}{l}$.

§ 92. Having found a series of particular solutions of the problem under consideration we have now to combine these together to form the general solution corresponding to any arbitrary initial state. For brevity we denote the proper function of x, by (262), by :

$$X_n = \cos \alpha_n x + \frac{b}{\alpha_n} \sin \alpha_n x \quad . \quad . \quad . \quad (266)$$

We multiply it by a constant A_n and by summation form the solution :

$$\theta = \sum_{n=1}^{\infty} A_n X_n e^{-a^2 \alpha_n^2 t} \quad . \quad . \quad . \quad (267)$$

To recognize that this is the general solution it is sufficient to prove that it can be adapted to an arbitrary given initial state (value of θ for $t = 0$), or that every given function $\theta_0(x)$ in the interval from $x = 0$ to $x = l$ can be expanded in a series of progressive proper functions :

$$\theta_0 = \sum_{n=1}^{\infty} A_n X_n \quad . \quad (268)$$

We shall here restrict ourselves to showing that unique values can be obtained for the coefficients A_n if $\theta_0(x)$ is given between $x = 0$ and $x = l$.

The method resembles that used in II, § 38, to expand a function $f(x)$ in a Fourier series, and actually in fact represents a generalization of it. For in the Fourier series the proper values of α are the whole multiples of $\frac{\pi}{l}$ and the proper functions are the series of the whole multiples of

$\frac{\pi x}{l}$, as can be seen directly by comparing the formula (268) with the special formula (258) derived in the preceding section for the case $b = \infty$.

As in II, § 38, so also here we multiply the given function θ_0 with a proper function X_n and then integrate with respect to x over the whole series of values between $x = 0$ and $x = l$. By (268) we then obtain :

$$\int_0^l \theta_0 X_n dx = \sum_{m=1}^{m=\infty} A_m \int_0^l X_m X_n dx \quad . \quad . \quad (269)$$

Here, as in the case of the Fourier series, the integral on the left must be directly calculated whereas the sum on the right reduces to a single term, namely that for which the index $m = n$. This happens in the following way in working out the integral on the right-hand side. Since the function X_n, by its definition (266), satisfies the differential equation :

$$\frac{d^2 X_n}{dx^2} = -\alpha_n^2 X_n \quad . \quad (270)$$

we have, intergrating by parts :

$$\int_0^l X_m X_n dx = -\frac{1}{\alpha_n^2}\int_0^l X_m \frac{d^2 X_n}{dx^2} dx$$

$$= -\frac{1}{\alpha_n^2}\left[X_m \frac{dX_n}{dx}\right]_0^l + \frac{1}{\alpha_n^2}\int_0^l \frac{dX_m}{dx} \cdot \frac{dX_n}{dx} \cdot dx$$

or :

$$\int_0^l \frac{dX_m}{dx} \cdot \frac{dX_n}{dx} dx = \alpha_n^2 \int_0^l X_m X_n dx + \left[X_m \frac{dX_n}{dx}\right]_0^l \cdot \quad . \quad (271)$$

If we exchange the indices m and n in this equation, the left-hand side remains unchanged, and consequently also the right-hand side, so that we get by subtraction :

$$(\alpha_n^2 - \alpha_m^2) \cdot \int_0^l X_m X_n dx = \left[X_n \frac{dX_m}{dx} - X_m \frac{dX_n}{dx}\right]_0^l \cdot$$

Now, by (253), (262) and (266) we have for $x = 0$:

$$\frac{dX_n}{dx} = bX_n \text{ and likewise } \frac{dX_m}{dx} = bX_m.$$

Hence the expression on the right-hand side vanishes for $x = 0$ and the same holds for $x = l$. Consequently :

$$\alpha^2_n - \alpha^2_m \cdot \int_0^l X_m X_n dx = 0 \quad . \qquad (272)$$

Thus if m and n are different from each other, we have generally :

$$\int_0^l X_m X_n dx = 0 \quad . \quad . \qquad (273)$$

which is the so-called "condition of orthogonality." The name recalls the analogously constructed formulæ I (332) and III (115) for the orthogonality of co-ordinates. Of the sum (269) only the term $m = n$ then remains :

$$A_n \int_0^l X_n^2 dx = \int_0^l \theta_0 X_n dx \quad . \qquad (274)$$

Here the integral on the left-hand side may either be calculated by substituting (266) in it and performing the integration, or indirectly as follows. From (271) it follows when $m = n$ that :

$$\int_0^l \left(\frac{dX_n}{dx}\right)^2 dx = \alpha_n^2 \int_0^l X_n^2 dx + \left[X_n \frac{dX_n}{dx}\right]_0^l \quad . \quad . \qquad (275)$$

On the other hand from (266) and the differential coefficient :

$$\frac{dX_n}{dx} = -\alpha_n \sin \alpha_n x + b \cos \alpha_n x \quad . \qquad (276)$$

we have, by squaring and adding, that :

$$\alpha_n^2 X_n^2 + \left(\frac{dX_n}{dx}\right)^2 = \alpha_n^2 + b^2 \, . \qquad (277)$$

or, integrated :

$$\alpha_n^2 \int_0^l X_n^2 dx + \int_0^l \left(\frac{dX_n}{dx}\right)^2 dx = (\alpha^2_n + b^2) l \quad . \quad . \qquad (278)$$

If we subtract the equations (275) and (278) from each other one of the integrals cancels out and we are left with :

$$2\alpha_n^2 \int_0^l X_n^2 dx = (\alpha_n^2 + b^2) l - \left[X_n \frac{dX_n}{dx}\right]_0^l$$

Now when $x = 0$ we have, by (266) and (276):

$$X_n = 1, \frac{dX_n}{dx} = b$$

whereas for $x = l$, we have, by (254), (262) and (266):

$$\frac{dX_n}{dx} = -bX_n$$

that is, by (277):

$$X_n^2 = 1$$

and:

$$X_n\frac{dX_n}{dx} = -bX_n^2 = -b.$$

So we have finally:

$$2\alpha_n^2\int_0^l X_n^2 dx = (\alpha_n^2 + b^2)l + 2b.$$

Substituting this value in (274) we get:

$$A_n \cdot \left[\frac{l}{2} + \frac{b^2 l}{2\alpha_n^2} + \frac{b}{\alpha_n^2}\right] = \int_0^l \theta_0 X_n dx\,. \tag{279}$$

In this way we have obtained the value of the coefficient A_n in the expansion of the function $\theta_0(x)$ in terms of the proper functions X_n and hence, by (267), our problem is solved.

§ 93. Hitherto we have assumed the body to be of infinite extent in the direction perpendicular to the x-axis. We shall now conversely investigate the heat conduction in a body in the form of a relatively long cylindrical rod which has a very small cross-section of any shape whatsoever, one of its ends being kept at a definite temperature θ_0 while the whole rod projects freely into a medium (air) which is at the constant temperature zero. (This is the experimental arrangement used by Wiedemann and Franz.) If we take the axis of the cylinder as our x-axis, the temperature in this case too essentially depends only on the co-ordinate x: this is, however, not because θ is independent of y and z, as in the cases hitherto treated, but because the co-ordinates y and

z have such small values for all points of the rod, so that θ varies only very little over a definite cross-section x of the cylinder.

In view of this circumstance we cannot neglect the differential coefficients with respect to y and z in the general differential equation (225) of heat conduction, but must take their values into account. This is done by setting up the boundary conditions which hold at the surface of the rod. These are, by (244):

$$q_\nu = -\kappa\frac{\partial\theta}{\partial\nu} = -h\theta$$

or:

$$\frac{\partial\theta}{\partial\nu} = b\theta \quad . \quad . \quad . \quad (280)$$

where ν denotes the inward normal to the surface. If we integrate the equation (225) for a constant x over the corresponding cross-section q of the rod, we get:

$$q\frac{\partial\theta}{\partial t} = a^2\frac{\partial^2\theta}{\partial x^2}\cdot q + a^2\iint\left(\frac{\partial^2\theta}{\partial y^2} + \frac{\partial^2\theta}{\partial z^2}\right)dy\,dz. \quad . \quad (281)$$

This double integral may be transformed, in a manner exactly analogous to that used in transforming the triple integral in II (82), by performing the integration and converting the integral into a contour integral, namely:

$$\iint\left(\frac{\partial^2\theta}{\partial y^2} + \frac{\partial^2\theta}{\partial z^2}\right)dy\,dz = -\int\frac{\partial\theta}{\partial\nu}\,d\lambda \quad . \quad . \quad (282)$$

where $d\lambda$ denotes the element of length, taken positively, of the contour of the cross-section. If we take into account the condition (280) that holds along the whole contour the double integral assumes the value:

$$-b\int\theta\,.\,d\lambda = -b\theta\,.\,\lambda$$

where λ now denotes the length of the contour. And the differential equation (281) assumes the form:

$$q\frac{\partial\theta}{\partial t} = a^2q\frac{\partial^2\theta}{\partial x^2} - a^2b\theta\lambda$$

or :

$$\frac{\partial \theta}{\partial t} = a^2 \frac{\partial^2 \theta}{\partial x^2} - f^2 \, . \, \theta \quad . \quad . \quad . \quad (283)$$

where we have set :

$$\frac{a^2 b \lambda}{q} = f^2 \quad . \quad . \quad . \quad (284)$$

or, by (224) and (245) :

$$f^2 = \frac{h\lambda}{ckq} \quad . \quad . \quad . \quad . \quad (285)$$

Thus the constant f depends on the specific heat of the substance, its specific gravity, the surface area and length of the contour of the cross-section and, finally, on the coefficient of external heat conduction h, but *not* on the coefficient of internal heat conduction κ. From this it follows that in the differential equation (283), which gives the variation of the temperature with the time, the influences of the internal and the external heat conduction are simply become added.

For the state which is *stationary* in time we get from (283) :

$$a^2 \frac{\partial^2 \theta}{\partial x^2} - f^2 \theta = 0$$

which, when integrated, gives :

$$\theta = A e^{\frac{fx}{a}} + B e^{-\frac{fx}{a}} \quad . \quad . \quad (286)$$

The boundary conditions at both ends of the rod serve to determine the two integration constants A and B. The one end ($x = 0$) is maintained at the constant temperature θ_0; so :

$$\theta_0 = A + B \quad . \quad . \quad . \quad . \quad . \quad (287)$$

The other end ($x = l$) projects freely into the air. For this we have the boundary condition (280) :

$$-\frac{\partial \theta}{\partial x} = b\theta$$

and hence, by (286), for $x = l$:

$$A\left(b + \frac{f}{a}\right)e^{\frac{fl}{a}} + B\left(b - \frac{f}{a}\right)e^{-\frac{fl}{a}} = 0 \quad . \quad . \quad (288)$$

Equations (287) and (288) determine A and B. If the length l of the rod is great compared with $\frac{a}{f}$, then, by (288), A vanishes compared with B; and, by (287), we get simply $B = \theta_0$.

PART THREE

HEAT RADIATION

CHAPTER I

INTENSITY OF RADIATION. EMISSION AND ABSORPTION

§ 94. THE equalisation of temperature in bodies at rest is effected not by heat conduction alone but also by heat radiation, which is a totally different mode of propagation of heat. For whereas the heat conduction in a body, as we saw in the second part of this book, is represented by a vector which is completely determined by the temperature gradient at the point and hence vanishes simultaneously with it, the radiant heat at a point is in itself quite independent of the temperature of the body at this point. Thus the radiation from the sun can pass through a lens made of ice and can be brought to a focus. Moreover the state of radiation at a definite point is not characterized by a single directed quantity but in general comprises an infinite number of rays which traverse the point in all possible directions, their intensity, frequency and polarization being entirely independent of one another. Further, two rays moving in diametrically opposite directions but having exactly the same frequency and polarization do not combine into a single resultant but behave as if entirely independent of one another.

We regard heat rays, just as we regarded optical rays in Volume IV, as electromagnetic waves, but for simplicity we shall restrict our investigations to those cases for which the laws of geometrical optics or ray optics (IV, § 28) hold, by excluding the phenomena of "diffraction" and "scattering." We also require to separate all lengths that come into question into two sharply differentiated groups according to their order of magnitude: the one group comprises wave-lengths, the other the linear dimensions of bodies. The former are vanishingly small compared with the latter and even compared with the differentials of the latter. It is only under this condition that we may assume the laws of ray optics to be valid. It is usually fulfilled if we assume the dimensions of the bodies under consideration to be sufficiently great.

But although the distinction between great and small lengths is as important in heat theory as in optics, the distinction between great and short times is still more important. For the very definition of the intensity of a beam of heat as that energy which is supplied by the beam per unit of time contains the assumption that the unit of time chosen is great compared with duration of the vibration corresponding to the colour of the beam (cf. IV, § 4). Otherwise the amount of the intensity of radiation would in general obviously depend on the phase of the vibration at which we begin to measure the energy provided by the beam. Only when the unit of time happened to include a whole number of vibrations would the intensity of a beam be of constant period and constant amplitude independent of the initial phase. To escape from this inconsistency we find ourselves compelled to postulate that the unit of time or, better, the time which is used to obtain the mean value of the radiant energy is great compared with the period of any of the vibrations contained in the beam.

§ 95. The great simplification which we gain by restricting ourselves to ray optics is due to the fact that it allows us to imagine the radiant energy to be localized in separate independent beams. On this view every body is filled with a group of energy rays, each of which describes its own definite path with a velocity which is determined by the index of refraction of the body; and each ray is refracted and reflected at the surface of the body according to the laws of optics (Fermat's Principle, IV, 91). An infinite number of rays pass through each definite point of the body, but only one passes through two definite given points. To be able to speak of the intensity of radiant energy we must start out not from two points but from two elements of area $d\sigma$ and $d\sigma'$ both of which we assume infinitely small compared with their distance apart, but otherwise arbitrary. In particular, one of the elements of area can be infinitely great compared with the other. From each point of the element $d\sigma$ a definite ray then goes to each point of the other element of area $d\sigma'$, and conversely. All these rays taken together form a four-fold infinity of rays, or a two-fold infinity of cones of rays with their vertices at $d\sigma$ or $d\sigma'$, which we call the beam or pencil of rays (*Strahlenbündel*) having the "focal surfaces" (*Brennflächen*) $d\sigma$ and $d\sigma'$. The focal surfaces which characterize the beam play a very important part in it. For if we intersect the beam at any point by means of any plane other than $d\sigma$ or $d\sigma'$ we can no longer speak of a definite cross-section of the beam; rather, each of the infinite number of conical beams with their vertices on $d\sigma$ or $d\sigma'$ has a distinctive cross-section.

If the body is homogeneous and isotropic, as we shall assume, the rays are straight and their velocity of propagation is the same in all directions. Then the energy which is radiated per unit of time by the beam of rays from $d\sigma$ through $d\sigma'$ will be proportional to the areas of the surface elements $d\sigma$ and $d\sigma'$ and inversely proportional to the square of the distance between them (III, § 90), but, further, it will also be proportional to the cosine of the (acute) angle which the direction of r makes with the directions of the normals ν and ν' to $d\sigma$ and $d\sigma'$ respectively. For the number of rays which belong to the beam is not determined by the quantities $d\sigma$ and $d\sigma'$ themselves but by their projection on the plane perpendicular to r, as is seen from simple geometrical considerations.

Thus we obtain for the energy which is radiated through the surface element $d\sigma$ in unit time to the surface element $d\sigma'$ the expression:

$$K \cdot \frac{d\sigma \,.\, d\sigma' \,.\, \cos(\nu, r) \,.\, \cos(\nu', r)}{r^2} \cdot dt \,. \qquad (289)$$

where K is the "specific intensity of radiation" or the "emissivity," a finite positive quantity, which in general depends on the space co-ordinates, time and direction. If, in particular, K is constant, the two surface elements $d\sigma$ and $d\sigma'$ radiate equal quantities of energy to each other, as is evident from the symmetry of the expression (289). If we introduce the quantity:

$$d\Omega = \frac{d\sigma' \,.\, \cos(\nu', r)}{r^2} \qquad (289a)$$

for the solid angle (*Öffnungswinkel*) which the surface element $d\sigma'$ appears to make when seen from a point of the surface element $d\sigma$, the expression for the energy which is radiated becomes still simpler:

$$K \,.\, d\sigma \cos(\nu, r) \,.\, d\Omega \,.\, dt$$

or, if we denote the angle which the direction r makes with the normal ν to $d\sigma$ by θ:

$$K \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt \quad . \quad . \quad . \qquad (290)$$

From this we see, among other things, that we can speak of a finite radiation of energy in a definite direction only in so far as the radiation occurs within a cone of finite aperture. There is no finite light or heat radiation which propagates itself in one direction only, or, what amounts to the same thing, there is in nature no absolutely parallel light, there are no absolutely plane waves of light. A finite amount of radiant energy can be obtained from a so-called parallel beam of rays only if the rays or the wave-normals of the beam diverge within a finite, even if only very small, cone (cf. IV, § 36).

A fundamental difference between light- and sound-waves is due to this circumstance, which, as we shall see later, is intimately connected with the fact that the second law is of importance only for optics, not for acoustics.

From (290) we see that the total radiation through the element of surface $d\sigma$ towards the one side is obtained by integrating with respect to θ from 0 to $\frac{\pi}{2}$ and with respect to ϕ from 0 to 2π, since $d\Omega = \sin\theta\, d\theta\, d\phi$:

$$d\sigma \,.\, dt \,.\, \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} d\theta\, K \sin\theta \cos\theta$$

where K is a given function of θ and ϕ. If the radiation is uniform in all directions, that is, if K is constant, it follows from this expression that the total radiation through $d\sigma$ towards one side is:

$$\pi K\, d\sigma\, dt \quad . \quad . \quad . \quad . \quad (291)$$

§ 96. Since the radiant energy propagates itself in the medium with the finite velocity q, if we leave out of account dispersion, a finite amount of energy exists in a finite part of space. We therefore speak of the "spatial energy density" u as the ratio of the total radiant energy contained in an element of volume to the magnitude of the element of volume. Let us now calculate the spatial density of radiation u at any point by assuming that the specific intensity of radiation K at this point is given as a function of θ and ϕ. With the point as centre describe a sphere, then all rays that intersect at the point will pass through the surface of the sphere; each of these rays contributes its portion to the required density of radiation u. The energy which is emitted in a time dt from a surface element $d\sigma$ of the sphere to a parallel surface element $d\sigma'$ which is infinitely great compared with $d\sigma$ and passes through the centre of the sphere is, by (289):

$$K \cdot \frac{d\sigma\, d\sigma'}{r^2} dt.$$

When this energy has reached the centre it fills the space of a rectangular parallelepiped whose area of base is $d\sigma'$ and height $q \,.\, dt$, that is, whose volume is $d\sigma' \,.\, qdt$. By dividing this into the expression just obtained for the energy we get for the spatial density of radiation produced by the beam at the centre of the sphere:

$$\frac{Kd\sigma}{qr^2} = \frac{K}{q} d\Omega$$

where $d\Omega$ denotes the solid angle which the element $d\sigma$ of the spherical surface appears to subtend at the centre. By integrating over all directions in space we obtain the required spatial density of the whole radiation at the point in question :

$$u = \frac{1}{q}\int K d\Omega = \frac{1}{q}\iint K \sin\theta \, d\theta \, d\phi \qquad (291a)$$

In the case of uniform radiation K is again constant, and so we get :

$$u = \frac{4\pi K}{q} \qquad (292)$$

§ 97. The specific intensity K of the radiant energy in every direction subdivides further into the intensities of the individual rays, which belong to the different parts of the spectrum and propagate themselves independently of one another, that is, into the rays of different "colours." The important factor that here enters is the intensity of radiation within a definite range of frequencies, say from ν to ν'. If the interval $\nu' - \nu$ is sufficiently small, equal to $d\nu$, then the intensity of radiation over this range is proportional to $d\nu$: the radiation is then called "homogeneous" or "monochromatic." But we must bear in mind that even in the case of such homogeneous radiation there is always a finite although small interval of frequencies corresponding to a finite amount of radiant energy.

The last characteristic of a ray, besides its definite intensity, direction and frequency ν is its type of polarization. If we denote the two principal intensities corresponding to the two mutually perpendicular principal planes of vibration (IV, § 11) by $K_\nu d\nu$ and $K'_\nu d\nu$, we get, if we sum up over the whole spectrum :

$$K = \int_0^\infty (K_\nu + K'_\nu) d\nu . \qquad (293)$$

where K_ν is now to be regarded as a finite function of the space co-ordinates, the time, the direction and the frequency ν.

For unpolarized rays $K_\nu = K'_\nu$, hence :

$$K = 2\int_0^\infty K_\nu d\nu \ . \qquad (294)$$

If further the radiation is uniform in all directions we get, by (291), for the total radiation through a surface element $d\sigma$ towards one side :

$$2\pi d\sigma dt \int_0^\infty K_\nu d\nu \quad . \qquad (295)$$

Just as we speak of the spatial density of the total radiation u so we also speak of the spatial density of the radiation of a definite frequency u_ν, by subdividing the spectrum thus :

$$u = \int_0^\infty u_\nu d\nu \qquad (296)$$

Combining the equations (292) and (294) we get for light which is unpolarized and uniform in all directions :

$$u_\nu = \frac{8\pi K_\nu}{q} \quad . \qquad (297)$$

§ 98. Hitherto we have dealt only with the propagation of radiant energy in a body. We shall now turn our attention to the birth and the annihilation of heat rays. The process of birth of a heat ray is generally called "emission." According to the energy principle the emission always takes place at the expense of some other energy (internal heat of bodies, chemical energy, electrical energy). From this it follows that only material particles, including electrical particles, can emit heat rays, but not geometrical spaces or surfaces. We commonly speak of the surface of a body emitting heat to its surroundings, but this expression only means that the rays which, coming from the interior of the body, impinge on the surface, are partly transmitted through the surface to the outside, the remainder being reflected back into the interior.

Let us now consider the interior of a physically homogeneous substance emitting rays and let us mark off some element of volume $d\tau (\gg \lambda^3)$. Then the total amount of radiant energy emitted in the time dt by all the particles in the element of volume will be proportional to $d\tau$. If the substance is isotropic the radiation will be emitted uniformly in all directions and the energy emitted within a cone will be proportional to the solid angle of the cone. Further, the radiation will be unpolarized. Hence the total energy emitted in the time dt by the element of volume $d\tau$ in the direction of the elementary cone $d\Omega$ and having frequencies between ν and $\nu + d\nu$ may be set equal to:

$$dt \, . \, d\tau \, . \, d\Omega \, . \, d\nu \, . \, 2\epsilon_\nu \quad . \quad . \quad . \quad . \quad (298)$$

We call the finite quantity ϵ_ν the coefficient of emission or emissivity of the substance for the frequency ν. It refers to a linearly polarized ray. The total emission of the volume element $d\tau$ is obtained by integrating over all directions and all frequencies. This leads to:

$$dt \, . \, d\tau \, . \, 8\pi \int_0^\infty \epsilon_\nu d\nu \qquad (299)$$

The emissivity ϵ_ν, besides depending on the frequency ν, also depends on the state of the emitting substance contained in the volume element; in general this dependence is very complicated. But in the sequel we shall everywhere introduce the simplifying assumption that the substance is in thermodynamic equilibrium in the element of space $d\tau$. It necessarily follows then that the emissivity ϵ_ν, besides depending on the density and the chemical nature of the substance, depends on nothing else except the temperature T and the frequency ν. In this case the radiation is called "temperature radiation" in contrast with "fluorescence radiation."

§ 99. The annihilation of a heat ray is called "absorption." According to the energy principle the energy of the radiation must be transformed in this process into some other form of energy (such as internal heat of bodies, chemical energy), and hence it follows that only material particles can absorb heat rays, but not surface elements, although we speak for the sake of brevity of absorbing surfaces.

The process of absorption manifests itself in the fact that a heat ray which is advancing through a medium is weakened in its passage to a fraction of its original intensity; for a sufficiently small distance s of its path this fraction is proportional to the length traversed. We shall set it equal to:

$$\alpha_\nu \cdot s \quad . \qquad . \quad (300)$$

and shall call α_ν the absorption coefficient of the substance for a ray whose frequency is ν. Since we are considering only homogeneous and isotropic substances we may assume α_ν to have the same value at all points and in all directions and to depend only on the frequency ν, the temperature T and the nature of the substance.

If α differs from zero only for a limited range of the spectrum the substance possesses "selective" absorption. For those colours for which $\alpha_\nu = 0$ the substance is completely transparent or "diathermanous." The properties of selective absorption and diathermancy may, however, vary greatly with the temperature. In general we assume α_ν to have a moderate magnitude; this implies that the absorption along a single wave-length is very weak. For the distance s, although small, yet contains many wave-lengths (§ 94).

If the radiation arrives at the boundary of the medium and there impinges on the surface of another medium, in general a part will be reflected, the remainder being allowed to pass through. Reflection and refraction either occur regularly, in accordance with the law of reflection and Snell's law of refraction (IV, § 8), or they occur "diffusely," that is, the rays are scattered at the surface in different directions with different intensities in the two media. In the former case we call the surface of the second medium "absolutely plane" or "smooth," in the latter we call it "rough." If a smooth surface completely reflects all the rays that fall on it we call it a "mirror surface." But if a rough surface completely reflects all the incident rays uniformly in all directions we call it "white." The converse limiting case in which the surface of a medium completely transmits all the incident rays does not occur in the case of smooth surfaces if the media in contact are optically different at all. Besides speaking of white surfaces we also speak of "black" surfaces. We call a body black when it absorbs all the incident rays, reflecting none and transmitting none. To be black a body must therefore fulfil two different and entirely independent conditions. *Firstly*, it must have a black surface. Since the properties of a surface are in general influenced by the substances on both sides of it this condition shows that the degree of blackness of a body depends not only on its own nature but also on the nature of the neighbouring medium. A body which is black for air need not be so for glass, and conversely. *Secondly*, the black body must have at least a certain thickness, which is determined according to the degree of its absorptive power, in order that the rays received by it may be completely absorbed in its interior and cannot again pass out through the surface at any other point. The more strongly a body absorbs the less will be the thickness necessary for complete absorption.

These distinctions and definitions in the first place refer only to rays of a definite colour. A surface, for example, which is rough for a certain kind of rays may be smooth for another kind of rays. In general a surface becomes less and less rough for rays of increasing wave-length, as is easy to understand. Since, as above remarked, smooth non-reflecting surfaces do not exist, all black surfaces that can be prepared in practice (lamp black, platinum black) exhibit appreciable reflection for rays of sufficiently great wave-length. Concerning the possibility of realising black bodies experimentally see § 104 below.

CHAPTER II

KIRCHHOFF'S LAW. BLACK BODY RADIATION

§ 100. We shall now apply the theorems worked out in the preceding chapter to the special case of thermodynamic equilibrium. We therefore preface our discussion by drawing the following inference from the second law: a system of bodies of any kind which are at rest and enclosed by an envelope impervious to heat passes in the course of time from any arbitrarily chosen initial state into a state of equilibrium for which the temperature in all the bodies of the system is the same. In this final state the entropy of the system has reached the maximum of all those values which it may assume with the total energy given by the initial conditions.

In certain cases it may happen that under the given conditions the entropy can assume not only one but several different maxima, one of which is the absolute maximum, whereas the others are of only relative importance. In these cases there are several different states of thermodynamic equilibrium. But of these only that, to which the maximum value of the entropy corresponds, denotes the absolutely stable state of equilibrium. The others are in a certain sense unstable or metastable, in that if the equilibrium is disturbed appropriately, be it ever so slightly, a permanent change of the system occurs in the direction of a more stable equilibrium. Cf. §§ 54 and 58 above.

We next enquire into the conditions which the radiation phenomena must obey to be in harmony with these laws. We therefore investigate the thermodynamic state of equilibrium of one or more bodies filled with radiation. First we take the simplest case, a single medium which extends very far in every direction of space and, like all other systems here to be considered, is surrounded by an envelope which is opaque to heat. Let us provisionally assume that the medium has a finite emissivity ϵ_ν and a finite absorption coefficient α_ν for every frequency ν.

We shall first consider those regions of the medium which are far removed from the surface. For them, at any rate, the influence of the surface becomes vanishingly small; and on account of the homogeneity and isotropic character of the medium we shall have to conclude that in the state of thermodynamic equilibrium the heat radiation is of the same quality everywhere and in all directions, or, by § 97, that $\mathfrak{K}_\nu$ is independent of the azimuth of the polarization, the direction and the space co-ordinates. Hence corresponding to every beam of rays which starts from a surface element $d\sigma$ and diverges within an elementary cone $d\Omega$ we must have an exactly similar beam travelling in the opposite direction and converging within the same elementary cone *towards* the surface element.

As the state of the radiation remains unchanged it follows immediately that during an arbitrary length of time just as much heat radiation is absorbed in every element of volume as is emitted; this applies to every frequency individually. For the different kinds of rays behave quite independently of one another, and the radiation of a definite frequency can be influenced in no other way than by emission or absorption. We calculate the energy emitted and absorbed during any time t within a volume element by fixing our attention on the radiation contained in a volume element within a definite elementary cone $d\Omega$. To simplify the calculation we choose the volume element in the form of a rectangular parallelepiped with its base $d\sigma$ perpendicular to the direction of the elementary cone and of height s, so that the volume

$d\tau = s \, . \, d\sigma$. Then the energy of the unpolarized radiation emitted is, by (298):

$$t \, . \, s \, . \, d\sigma \, . \, d\Omega \, . \, d\nu \, . \, 2\epsilon_\nu .$$

On the other hand the radiation that enters the volume element through its base $d\sigma$ is, by (290) and (294):

$$t \, . \, d\sigma \, . \, d\Omega \, . \, 2K_\nu \, . \, d\nu$$

and of this the fraction $\alpha_\nu \, . \, s$ is absorbed in the distance s, by (300). If we multiply the last expression by $\alpha_\nu \, . \, s$ and set this product equal to the expression given just above, we get as the condition of equilibrium:

$$K_\nu = \frac{\epsilon_\nu}{\alpha_\nu} \tag{301}$$

That is, *in the interior of a medium which is in thermodynamic equilibrium the specific intensity of radiation corresponding to each vibration number is equal to the quotient of the emissivity and the absorption coefficient of the medium for the frequency concerned.* Since ϵ_ν and α_ν depend, in addition to the nature of the medium, only on T and ν, the intensity of radiation of a definite colour in a definite medium is completely determined, in thermodynamic equilibrium, by the temperature.

An exception occurs, however, when $\alpha_\nu = 0$, that is when the medium does not absorb the colour in question at all. Since K_ν cannot become infinitely great, it follows that in this case also $\epsilon_\nu = 0$; that is, a medium emits no colour which it does not absorb. Further we see that when ϵ and α vanish simultaneously the equation (301) is satisfied by *every* value of K. *Hence in a medium of given temperature which is diathermanous for a definite colour thermodynamic equilibrium can exist for any arbitrary intensity of radiation of this colour.*

Here we already have an example of the cases discussed above, in which for a given total energy of a system adiabatically enclosed several states of equilibrium are possible corresponding to the different relative maxima of the entropy. For since the intensity of radiation of the colour in question in thermodynamic equilibrium is quite independent of the temperature of the medium which is diathermanous for it, the given total energy may be distributed quite arbitrarily over the radiation of that colour and the heat of the body without the equilibrium becoming impossible. Among all these distributions there must, however, be a perfectly definite one which corresponds to the absolute maximum of the entropy and which denotes absolutely stable equilibrium. This distribution, in contrast with the rest, which are in a certain sense unstable, has the property that it undergoes no appreciable change when subjected to a very small disturbance. We shall actually see below (§ 105) that among the infinite number of values which the quotient $\frac{\epsilon_\nu}{\chi_\nu}$ may assume when both the numerator and the denominator vanish, there is one special value which depends in a definite way on the nature of the medium, the frequency ν and the temperature. This particular value is to be called the stable intensity of radiation K_ν at the temperature in question in the medium which is diathermanous for the frequency ν.

What has been stated for a medium which is diathermanous for a definite frequency holds equally well for an absolute vacuum, as this is diathermanous for *all* colours, except that in this case we cannot speak of the heat of the body or of the temperature of the medium. For the present, however, we shall not deal with the special case of diathermancy at all but shall assume that the medium has a finite absorption coefficient.

§ 101. All the theorems so far deduced apply to only such parts of the medium as are at a very great distance from the surface, since it is only for them that we may immediately assume the radiation to be independent of position and direction. But a simple reflection shows that the value for K_ν calculated in (301) is also valid right up to the surface of the medium. For in thermodynamic equilibrium every beam of rays must have exactly the same intensity as the exactly opposite beam; otherwise a one-sided transport of energy would be brought about by the radiation. If therefore we fix our attention on a beam coming from the surface of the medium, it must have the same intensity as the exactly opposite beam coming from the interior. Hence it follows immediately that *the whole state of radiation of the medium at the surface is the same as in the interior.*

But although the radiation which starts from an element of the surface and is directed towards the interior of the medium is in every way the same as the radiation which is propagating itself at great distances from the surface, it nevertheless has a different history. For since the surface has been assumed to be opaque to heat rays, it can only have arisen owing to radiation which has come from the interior and been reflected at the surface. This can occur in many different ways according to whether the surface is assumed to be smooth, in this case mirror-like, or rough, say white. In the former case there corresponds to every beam of rays incident on the surface a perfectly definite reflected beam which is situated symmetrically with respect to it and has the same intensity. In the second case, however, each incident beam splits up into an infinite number of reflected beams of different intensity, direction and polarization, but always in such a way that the beams which come from all directions with the same intensity K_ν when reflected by the surface again produce as a whole a uniform radiation of the same intensity which propagates itself towards the interior.

Nothing now stands in the way of revoking the assumption made in § 100 that the medium in question must be of very great extent in all directions. For by the result just obtained the thermodynamic equilibrium of an infinitely extended medium is in no wise disturbed if we imagine any number of fixed surfaces, smooth or rough, which are impervious to heat to be placed in it. This divides the whole system up into an arbitrarily great number of completely closed systems, each of which can be taken as small as we please. From this it follows that the value given for the specific intensity of radiation K_ν in (301) also holds for the thermodynamic equilibrium of a body of *any* size and form.

§ 102. We shall now turn to the question of the equilibrium of radiation in a diathermanous medium, for which equation (301) fails, since $\alpha_\nu = 0$ and $\epsilon_\nu = 0$. The fact that a perfectly definite state of radiation also exists for such a medium at every temperature when there is thermodynamic equilibrium is shown by the following reasoning. We completely surround the medium with different kinds of fixed walls of any material whatsoever, which we choose so thick that no heat rays can penetrate through the walls either from the inside or from the outside; and we keep the walls at a definite uniform temperature. Then, on account of the consequent definite emission and absorption of the walls, a perfectly definite stationary state of radiation will establish itself in the medium. This will correspond to the state of stable thermodynamic equilibrium and will be determined by the temperature alone, and so will be independent of the material of the walls. This reflection allows us not only to calculate the state of the radiation in the medium, but also to establish a general relationship which must hold between the emission and the absorption of each individual wall in order that the radiation within the medium may become independent of the material of the wall. For simplicity we shall assume the surfaces of all the different walls to be smooth.

After thermodynamic equilibrium has been established we have by (290) and (294) the following expression for the energy of the unpolarized radiation lying within the range denoted by the frequencies ν and $\nu + d\nu$ and which coming from the interior of the medium impinges in the time dt on the surface element $d\sigma$ of a wall within the elementary cone $d\Omega$ at an angle θ to the normal to the surface:

$$2K_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt = 2J_\nu \,.\, d\sigma \,.\, dt \quad . \qquad (302)$$

where J_ν refers to a linearly polarized radiation. The same amount of energy is radiated in the reverse direction back into the medium. The latter amount of energy is composed of the energy emitted by $d\sigma$ and of that reflected by $d\sigma$. The energy emitted will be of the form :

$$2E_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt \quad . \quad . \quad . \qquad (303)$$

where E_ν, the " emissive power " of the material of the wall, signifies a definite finite quantity in general also dependent on the direction θ.

The reflected energy comes from the beam of rays of intensity J_ν which lies symmetrically with respect to the normal to the surface and falls on $d\sigma$; after reflection it becomes the beam in question and has the energy :

$$\rho_\nu \,.\, 2J_\nu \,.\, d\sigma \,.\, dt \quad . \quad . \quad . \quad . \quad . \qquad (304)$$

where ρ_ν denotes the reflection coefficient of the wall for the direction in question.

If we set the sum of the expressions (303) and (304) equal to the expression (302) we get :

$$K_\nu = \frac{E_\nu}{1 - \rho_\nu}$$

or, if we set :

$$1 - \rho_\nu = A_\nu$$

where A_ν, the " absorbing power " of the wall, denotes the fraction of the incident radiant energy that penetrates into the wall, we get :

$$K_\nu = \frac{E_\nu}{A_\nu} \quad . \qquad (305)$$

For different walls E_ν and A_ν are different, but their ratio is always equal to K_ν. This is Kirchhoff's Law, which states that *the ratio of the emissive power of a body to its absorptive power is independent of its nature.*

From this we see that even for any diathermanous body there is a definite specific intensity of radiation K_ν for each temperature when there is thermodynamic equilibrium; and K_ν is obtained by dividing the emissive power of any substance which is in contact with the body by its absorptive power. We may also call this value of K_ν the "true value" of the quotient (301) for $\alpha_\nu = 0$. The relation (305) of course also holds for the case where the medium emits and absorbs to a finite degree. The method of proof follows exactly similar lines.

For a black wall $\rho_\nu = 0$ and $A_\nu = 1$, hence $K_\nu = E_\nu$. That is, *the emissive power of a black body is independent of its nature and is equal to the stationary specific intensity of radiation in the contiguous medium.* Hence this radiation is often shortly called "black body radiation" or "black radiation." Further, since $A_\nu < 1$, the emissive power of a black body is always greater than that of any other body.

§ 103. All the relations deduced in the preceding paragraph hold for a single definite medium traversed by the radiation. But we can also generalize them so that they become applicable to arbitrary media and acquire a universal character. This is performed by bringing into contact two different media, say air and glass, which are traversed by radiation, and investigating the stationary state which corresponds to thermodynamic equilibrium. Since the equilibrium is in no way disturbed if we imagine the plane of separation of the two media to be replaced by a surface which is impervious to heat radiation, all the results of § 101 apply. Let the specific intensity of the linearly polarized radiation of frequency ν in the interior of the first medium (air, in Fig. 7 on the left) be K_ν, and that in the interior of the second medium (glass, on the right of Fig. 7) be called K'_ν; we shall denote all quantities referring to the second medium by a dash, as in the case of K'_ν. Both quantities K_ν and K'_ν, besides depending on the temperature and the frequency, depend only on the nature of the two media. Moreover, these values of the intensity of radiation hold right up to the bounding surface, quite independently of the nature of this surface.

We next assume the bounding surface to be smooth and fix our attention on some monochromatic linearly polarized radiation. The energy of this radiation which is emitted during the time dt by an infinitely small element $d\sigma$ at the point O of the bounding surface within the elementary cone $d\Omega$ at an angle θ with the normal to the surface is, in air (upwards towards the left in the Fig.), by (302):

$$K_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt \quad . \tag{306}$$

where:

$$d\Omega = \sin\theta\, d\theta\, d\phi \tag{307}$$

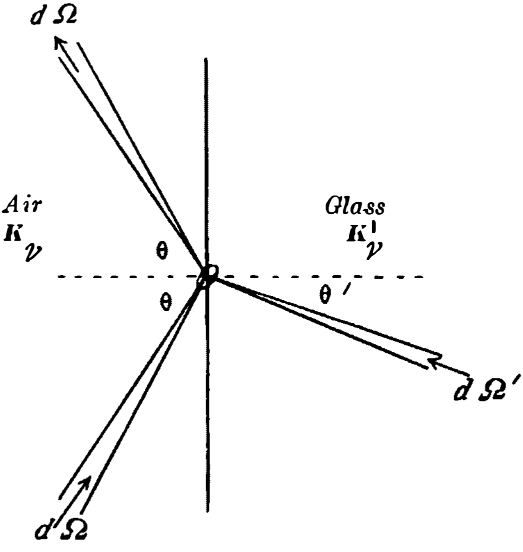

FIG. 7.

This energy is furnished by the two beams which, coming from the air (on the left) and the glass (on the right), respectively, are reflected by the surface element $d\sigma$ or are refracted. The former beam travels along inside the symmetrically situated cone $d\Omega$, the latter inside the cone:

$$d\Omega' = \sin\theta'\, d\theta'\, d\phi' \quad . \tag{308}$$

the law of refraction giving:

$$\phi' = \phi \text{ and } \frac{\sin\theta}{\sin\theta'} = \frac{q}{q'} \; . \tag{309}$$

The contribution of the former beam to the energy is, by (306):

$$\rho_\nu \,.\, K_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt \,. \quad . \quad . \qquad (310)$$

where ρ_ν again denotes the reflection coefficient for the radiation in question from glass in air. On the other hand the contribution of the latter beam of radiation to the energy is:

$$(1 - \rho'_\nu) \,.\, K'_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta' \,.\, d\Omega' \,.\, dt \quad . \qquad (311)$$

where ρ'_ν denotes the reflection coefficient and hence $1 - \rho'_\nu$ the transmission coefficient for glass in air.

If we add the last two expressions together and set the sum equal to the expression (306), we get:

$$\rho_\nu \,.\, K_\nu \,.\, \cos\theta \,.\, d\Omega + (1 - \rho'_\nu) \,.\, K'_\nu \cos\theta' \, d\Omega' = K_\nu \cos\theta \,.\, d\Omega$$

Now, by 309:

$$\frac{\cos\theta \,.\, d\theta}{q} = \frac{\cos\theta' \,.\, d\theta'}{q'}$$

and if (307) and (308) are taken into account:

$$\frac{d\Omega' \cos\theta'}{q'^2} = \frac{d\Omega \,.\, \cos\theta}{q^2}$$

Consequently:

$$\rho_\nu K_\nu + (1 - \rho'_\nu) \, K'_\nu \frac{q'^2}{q^2} = K_\nu$$

or:

$$\frac{q^2 \,.\, K_\nu}{q'^2 \,.\, K'_\nu} = \frac{1 - \rho'_\nu}{1 - \rho_\nu}$$

In this equation the quantity on the left is independent of the angle of incidence θ and of the nature of the polarization; consequently so is the expression on the right-hand side. Hence if we know its value for a single angle of incidence and a definite azimuth of the polarization this value holds good for all angles of incidence and all directions of polarization. Now in the special case when the rays vibrate in the plane of incidence and fall on the bounding surface at the angle of polarization we have $\rho_\nu = 0$ and $\rho'_\nu = 0$ (IV, § 9*a*). The expression on the right then becomes equal to 1. Hence it is in general equal to 1, and we always have:

$$\rho_\nu = \rho'_\nu \qquad (312)$$

and:

$$q^2 K_\nu = q'^2 K'_\nu \qquad (313)$$

The first of these two relations, which states that the reflection coefficient of the bounding surface is the same towards both sides, expresses for a special case a general law of reciprocity which was first proved by Helmholtz; it states that the loss of intensity which a ray of definite colour and polarization experiences in its passage through any media owing to reflection, refraction and absorption is exactly equal to the loss of intensity which a ray correspondingly constituted experiences when travelling in the exactly opposite direction. From this it follows directly that the boundary surface of two media is equally transparent in both directions and reflects equally well on both sides for every colour, direction and kind of polarization.

The second relation, (313), brings into relationship the intensities of the black body radiation in the two media. It states that in thermodynamic equilibrium the specific intensities of radiation of a definite frequency in the two media are inversely proportional to the squares of the velocities of propagation or directly proportional to the squares of the indices of refraction.

If we substitute the value for K_ν from (301), we may also say, *the quantity*:

$$q^2 K_\nu = q^2 \frac{\epsilon_\nu}{\alpha_\nu} = F(\nu, T) \qquad (314)$$

does not depend on the nature of the medium; hence it is a universal function of the temperature T and the frequency ν. To find this universal function F is the fundamental problem of the theory of heat radiation. In view of (297) we may also formulate this theorem as follows: the quantity:

$$u_\nu q^3 \qquad (315)$$

is, for thermodynamic equilibrium, identically the same function of the temperature T and the frequency ν for all substances. Or, since $q = \lambda\nu$, we may say that in the case of black body radiation the energy contained in a cube whose length of side is the wave-length λ, namely:

$$u_\nu \, . \, d\nu \, . \, \lambda^3 \qquad \text{. . . . .} \qquad (316)$$

is the same for all bodies.

§ 104. The laws deduced in the preceding pages also enable us to measure the emissive power of a black body in spite of the fact that absolutely black bodies do not exist in nature (§ 99). We form a diathermanous cavity bounded by walls which emit more or less strongly and are kept at a certain constant temperature T. Then, when thermodynamic equilibrium has been established, the radiation in the cavity acquires for each frequency the intensity K_ν which is conditioned by the velocity of propagation q in the medium, as given by the universal function (314). If we now make a hole of size $d\sigma$ in one of the walls, so small that the intensity of the radiation directed from the interior towards the hole is not changed, then radiation will pass through the hole to the outside where we may assume the same diathermanous medium to exist as in the interior, and this radiation will have exactly the same properties as if $d\sigma$ were the surface of a black body of temperature T.

There is only *one* medium which is diathermanous for *all* kinds of rays; that is an absolute vacuum, which, however, can be produced only approximately in nature. Yet many gases, for example atmospheric air, if not too dense, have very approximately the optical properties of a perfect vacuum. Hence in the sequel we shall as a rule write in place of q the value of the velocity of light c in a vacuum.

§ 105. As we have already seen in § 100 *any* arbitrary state of radiation can be stationary from the very outset in a perfect vacuum enclosed by totally reflecting walls. But as soon as one of the walls or even an arbitrarily small part of a wall manifests even the slightest emissive or absorptive power for a colour, or as soon as we introduce into the cavity space even the smallest quantity of any substance which absorbs or emits rays of some colour, then in the course of time a stationary state of radiation will establish itself in the whole cavity; this state will be such that the radiation of the colour in question will have the intensity K_ν which is determined by the universal function (314) and which corresponds to the temperature of the part of the wall in question or of the substance introduced. If this substance is completely diathermanous for no colour at all, for example, a piece of charcoal, then in the stationary state the intensity of all colours will be K_ν, namely that corresponding to black body radiation at the temperature of the substance. Regarded as a function of ν the quantity K_ν gives the spectral distribution of black body radiation *in vacuo* or the so-called *normal energy spectrum.* In the normal spectrum, since it is the emission spectrum of a black body, the intensity of radiation for any colour is the greatest that a body can emit at the temperature in question. By determining the normal energy spectrum we immediately arrive at the universal function (314).

Thus we can transform any radiation contained in an evacuated cavity enclosed by totally reflecting walls into black body radiation by simply introducing a tiny speck of charcoal. A characteristic feature of this process is that the "body heat" of the speck of charcoal can be arbitrarily small compared with the energy of radiation that is present in the cavity, for this may be assumed to be as large as we please; hence in this case the total radiant energy remains essentially constant even when the transformation to black body radiation is occurring, since the changes in the contained heat of the charcoal particle do not come into consideration even for finite changes of temperature of the particle. The particle then merely plays the part of a releasing agent; by absorption and emission it gives the impulse to the process of give and take which changes the intensities of the beams of radiation of different frequencies, differently polarized and travelling in different directions in the original radiation; this corresponds to the transition of the system from a less stable to a more stable state, or from a state of smaller to a state of greater energy. From the thermodynamic point of view this process is fully analogous to the change which a tiny spark produces in a quantity of electrolytic gas (H_2 and O_2) or a tiny drop of liquid produces in a quantity of super-saturated vapour or, again, that a catalyser produces in a mixture which has a slow rate of reaction. For the time of the transformation does not count: all that matters is that the manner and the magnitude of the disturbance should be exceedingly small so that they can be entirely neglected in comparison with the quantity of the energies transformed as well as with the increase of entropy of the system. In the case of heat radiation the essential feature of the particle of charcoal is its function as an indicator of temperature, for without it we should have no means of defining a temperature.

CHAPTER III

PRESSURE OF RADIATION. THE STEFAN-BOLTZMANN LAW

§ 106. THE next step towards finding the universal function (315) consists in applying the two fundamental laws of thermodynamics to black body radiation in a vacuum of variable volume. For this system can be treated according to exactly the same methods as a material body, say a gas, because the validity of the two laws is independent of the nature of the system under consideration. To make the calculation fruitful we must above all know the mechanical force which the radiation exerts on a wall with which it is in communication; just as we must know the equation of state of a gas if we wish to apply the two fundamental laws to gases. Let us then first consider the mechanical pressure which any plane electromagnetic wave *in vacuo* exerts on a black body on whose surface it impinges at an angle θ. For this purpose we may use the formulæ III (230) which give the mechanical pressure exerted by an electromagnetic field. Actually these formulæ were there deduced only for the case of an electrostatic field, but they also apply more generally, because the derivation of the pressure involved only the momentary state of the field and not its variation with the time. If we choose the inward normal of the surface of the body as our positive ξ-axis, as in IV, § 6, Fig. 1, the pressure in the direction of the normal, which alone comes into question, is, by the above-mentioned formulæ:

$$p = -\frac{1}{8\pi}(2E_\xi^2 - E^2) = \frac{1}{8\pi}(E_\eta^2 + E_\zeta^2 - E_\xi^2)\,. \qquad (317)$$

The expressions for E_ξ, E_η, E_ζ are given in IV, § 6, and we must note here that since the body is black there is an incident but no reflected wave, so that we now have :

$$\begin{aligned} E_\xi &= E_x \cos\theta - E_y \sin\theta = -f \, . \sin\theta \\ E_\eta &= E_x \sin\theta + E_y \cos\theta = f \, . \cos\theta \\ E_\zeta &= E_z = g \end{aligned}$$

where f and g denote the wave-functions of the wave-components that vibrate in directions parallel and perpendicular to the plane of incidence. Substitution in (317) gives :

$$p = \frac{1}{8\pi} \cdot (\overline{f^2} \cos^2\theta + \overline{g^2} - \overline{f^2} \sin^2\theta) \quad . \quad (318)$$

The mean values indicated by the bars must be taken because the radiation pressure, like the radiation energy, is defined only for a time which is great compared with that of a vibration (§ 94).

In addition to the pressure of the electric field we have also the pressure of the magnetic field which is given by the analogous formulæ III (239), thus :

$$p = \frac{1}{8\pi} (H_\eta^2 + H_\zeta^2 - H_\xi^2)$$

with the corresponding values :

$$\begin{aligned} H_\xi &= H_x \cos\theta - H_y \sin\theta = g \sin\theta \\ H_\eta &= H_x \sin\theta + H_y \cos\theta = - g \cos\theta \\ H_\zeta &= H_z = f. \end{aligned}$$

This gives :

$$p = \frac{1}{8\pi} (\overline{g^2} \cos^2\theta + \overline{f^2} - \overline{g^2} \sin^2\theta)$$

Adding this to (318) we get as the total pressure of the wave in question on the black body :

$$p = \frac{1}{4\pi} (\overline{f^2} + \overline{g^2}) \cos^2\theta \quad . \quad (319)$$

For an unpolarized wave we have $\overline{f^2} = \overline{g^2}$ and :

$$p = \frac{1}{2\pi} \overline{f^2} \cos^2\theta \quad . \quad . \quad (320)$$

We shall now bring the pressure into relationship with the radiation that falls on the surface element $d\sigma$ of the body, firstly for the case of a monochromatic beam. By IV (11), for an unpolarized plane wave *in vacuo* the energy radiated in the time dt on to a cross-section F perpendicular to the direction of the ray is in general :

$$\frac{c}{2\pi}\overline{f^2} \, . \, F \, . \, dt$$

that is, since $F = d\sigma \, . \, \cos\theta$, the radiant energy incident on the surface element $d\sigma$ is :

$$\frac{c}{2\pi}\overline{f^2} \cos\theta \, . \, d\sigma \, . \, dt.$$

We set this amount of energy equal to the energy given in (302) for an incident monochromatic beam. Then from (320) we get :

$$p = \frac{2J_\nu \cos\theta}{c} \qquad (321)$$

for the pressure of unpolarized monochromatic radiation incident on a black body at an angle θ.

If the body is a perfect reflector there must be added to the incident wave the reflected wave, whose intensity and energy, when added to the first, double the pressure :

$$p = \frac{4J_\nu \cos\theta}{c}. \qquad (322)$$

§ 107. From this we now calculate the pressure which any arbitrary radiation incident uniformly in all directions exerts on a perfectly reflecting surface. By integrating (322) over all directions and all frequencies, that is, by substituting the value of J from (302), we get :

$$p = \frac{4}{c}\iint K_\nu \, . \, \cos^2\theta \, . \, d\Omega \, d\nu$$

and since $d\Omega = \sin\theta \, d\theta \, d\phi$ we get by using (294) and integrating with respect to ϕ from 0 to 2π and with respect to θ from 0 to $\frac{\pi}{2}$:

$$p = \frac{4\pi K}{3c} \qquad (323)$$

or, if instead of K we introduce the spatial density of radiation u from (292):

$$p = \frac{u}{3} \quad . \qquad (324)$$

This value for the radiation pressure at present holds only for a perfectly reflecting wall. But it is easy for us to convince ourselves that it always holds if the radiation which leaves the wall is the same as the incident radiation; that is, if it makes no difference whether the radiation is reflected by the wall or emitted by it. For if we imagine a cavity space filled with black body radiation and completely surrounded by any walls at a uniform temperature but free to move as a whole, then it is not only in thermodynamic equilibrium but also in mechanical equilibrium, as otherwise we should be deriving mechanical energy from heat without compensation, which is contrary to the second law. From this it follows that the pressure of radiation is the same on all the enclosing walls no matter whether they are good or bad reflectors, so long as the radiation occurs uniformly in all directions.

§ 108. Let us next imagine an evacuated enclosure filled with black body radiation but of variable volume, say in the form of a cylinder with a perfectly fitting freely movable piston. For the radiation to remain continuously black during the changes of state which are to be effected, it is sufficient to assume any part of the enclosing wall, say the bottom of the cylinder, as emitting and, further, to allow the changes to take place infinitely slowly so that the changes in the direction of motion of the piston may take long enough to let the radiation get steady again. The energy density u of the black body radiation is then determined by the temperature T of the emitting wall. This is a system whose state depends on two variables, namely the volume V and the temperature T; it can be subjected to any arbitrary reversible changes. The system has the energy $U = V . u$ which depends on the temperature and which, on account of the radiation pressure p, can be used to perform mechanical work. Hence the condition (82) of the second law must be obeyed :

$$\frac{dU + pdV}{T} = dS \quad . \quad . \quad . \qquad (325)$$

This states that the entropy of cavity radiation depends only on the momentary state in question, that is on V and T.

Since the quantities U, p, V, S are all properties of the state of radiation, so also is T; that is, black body radiation also has a definite temperature, namely the temperature of the enclosing wall with which its exchange of heat is stationary.

To introduce the two independent differentials dT and dV in the differential expression (325) we set, since u depends only on T :

$$dU = d(V\,.\,u) = V\frac{du}{dT}dT + udV$$

and, in view of (324), obtain :

$$dS = \frac{V}{T}\frac{du}{dT}dT + \frac{4u}{3T}dV$$

From this, we get :

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{4u}{3T}.$$

If we differentiate the first equation partially with respect to V, the second partially with respect to T, we get :

$$\frac{du}{dT} = \frac{4u}{T}$$

which, integrated, leads to :

$$u = aT^4 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (326)$$

By (292) the specific intensity of the black radiation is :

$$K = \frac{c}{4\pi}u = \frac{ac}{4\pi}T^4 \quad . \quad . \qquad (327)$$

Consequently the total emission from unit surface of a black body is in unit time, by (291):

$$\pi K = \frac{ac}{4} T^4 = \sigma T^4 \quad . \quad . \quad . \quad (328)$$

Also, the pressure of black radiation is:

$$p = \frac{a}{3} T^4 \quad . \quad . \quad . \quad . \quad . \quad (329)$$

and the total energy of radiation:

$$U = aT^4 . V \quad . \quad . \quad . \quad . \quad . \quad . \quad (330)$$

This is the Stefan-Boltzmann law of black radiation. The value of the constant σ in (328) is, according to the best measurements hitherto made:

$$\sigma = \frac{ac}{4} = 5{\cdot}75 . 10^{-5} \text{erg/cm.}^2 \text{sec. degree}^4 \quad (331)$$

The value of the entropy S of the black radiation, which is obtained by integrating the differential equation (325), is:

$$S = \frac{4}{3} aT^3 V \quad . \quad . \quad . \quad . \quad . \quad . \quad (332)$$

if when $T = 0$ and $U = 0$ we also assume $S = 0$. From this it follows that the entropy per unit volume or the spatial entropy density of black radiation is:

$$\frac{S}{V} = s = \frac{4}{3} aT^3 \quad (333)$$

§ 109. If while the cavity is being increased in volume the temperature of the enclosing walls is kept constant, the process takes place *isothermally*. Then, besides T, also u, p and s remain constant. Consequently the total energy of the radiation increases from $U = V . u$ to $U' = V' . u$, the entropy increases from $S = V . s$ to $S' = V' . s$, and we get for the heat Q that is to be taken up from outside, by integrating (49), keeping T constant:

$$Q = \frac{4}{3} aT^4(V' - V) = \frac{4}{3}(U' - U)$$

We observe that the heat taken up from outside exceeds the amount by which the energy of radiation increases, $U' - U$, by the fraction $\frac{1}{3}(U' - U)$. This additional amount of heat is necessary to perform the external work involved in reversibly enlarging the volume of the radiation.

Let us also consider an *adiabatic* process. For this purpose it is necessary to assume that the whole enclosing wall of the cavity is either a perfectly reflecting mirror or, better still, is perfectly white. The heat taken up from outside during the volume change is then $Q = 0$, and the energy of the radiation changes only by the amount of external work done, $p \, . \, dV$. To be certain, however, that the radiation actually remains black during a finite adiabatic process, that is, that it retains its normal distribution of energy even when the energy density is changed, we shall further assume that a very small particle of charcoal is present in the cavity. This little body, which we may assume to have a finite absorptive power for every kind of ray, serves the sole purpose of bringing about the stable state of radiation (§ 105) and so guarantees the reversibility of the process, while its contained heat may be assumed to be vanishingly small compared with the energy of radiation U. The radiation is then at every instant equal to that of the charcoal particle.

During the reversible adiabatic change in question the entropy S of the system remains constant, and so by (332):

$$T^3 \, . \, V = \text{const.}$$

or by (329):

$$p \, . \, V^{\frac{4}{3}} = \text{const.}$$

That is, during adiabatic compression the temperature and the pressure of the radiation increase in a manner definitely specified. The energy U changes during the same process according to the law:

$$\frac{U}{T} = \frac{3}{4} S = \text{const.}$$

That is, it increases proportionally to the temperature T although the volume becomes smaller.

Finally let us consider the simple case of an *irreversible* process. Let the cavity of volume V, surrounded by perfectly reflecting walls, be uniformly filled with black body radiation. Now let us make an opening at some point in the walls, say by opening a tap, through which the radiation can enter into an evacuated space of larger dimensions and also enclosed by perfectly reflecting rigid walls. After a time the radiation will again become uniformly distributed over all directions and will uniformly fill the connected cavities, whose combined volume is V', say. Let us assume a charcoal particle present to ensure that all conditions for black radiation are also fulfilled in the new state. Since neither external work nor transference of heat from outside comes into question, we have by the first law of thermodynamics that $U' = U$, and hence by (330):

$$T'^4V' = T^4V$$

or:

$$\frac{T'}{T} = \sqrt[4]{\frac{V}{V'}},$$

which defines the new state of equilibrium. Since $V' > V$, the temperature of the radiation becomes lowered by the process.

According to the second law the entropy of the system must have increased. By (332) we actually have:

$$\frac{S'}{S} = \frac{T'^3V'}{T^3V} = \sqrt[4]{\frac{V'}{V}} > 1 \quad . \qquad (334)$$

If radiation of volume V is expanded adiabatically and irreversibly to the volume V' as above described but with no charcoal particle present, then after the state of radiation has become uniform in all directions in the new volume V' the radiation will no longer have the character of black radiation and so will have no definite temperature. But nevertheless the radiation, as indeed every physical system in a definite state, will have a definite entropy which, by the second law, will be greater than the initial entropy S, but not so great as that, S', expressed in (334). We shall show how it is calculated in the next chapter. If we subsequently introduce a charcoal particle into the vacuum, the absolutely stable state of equilibrium of the radiation will establish itself by means of a second irreversible process, the energy assuming the normal energy distribution for constant total energy U and constant total volume V', while the entropy attains its maximum value S' given by (334).

CHAPTER IV

ENTROPY AND TEMPERATURE OF A BEAM OF RADIATION. WIEN'S DISPLACEMENT LAW

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§ 110. The Stefan–Boltzmann Law deals with the total energy of stationary cavity radiation, but it gives no information about the spectral distribution, that is, about the form of the universal function (314). To find this we must make use of the theorem that the normal distribution of energy is the most stable of all possible energy distributions; in other words, it is that which makes the entropy of the radiation for given total energy and given volume a maximum. This theorem becomes fruitful only if the entropy of a radiation having any arbitrary distribution is known. Hence the solution ultimately depends on finding the entropy of any arbitrarily given radiation.

Now every radiation consists of a system of individual beams of rays of different direction, colour and polarization, which act quite independently of one another. Hence the entropy of the radiation is composed by adding together the entropies of all these individual beams. Each beam of definite intensity and frequency has a definite entropy which it carries along with it. Hence we can speak of an entropy radiation just as well as of an energy radiation, and this entropy radiation will propagate itself according to the laws of geometric optics. Corresponding to the specific intensity K_ν of the energy of a monochromatic linearly polarized beam there is the specific intensity L_ν of the entropy of this beam, where L_ν is a definite function of K and ν; and corresponding to the energy of the beam which is incident on, or emitted by, a surface element $d\sigma$ (§ 102) during the time dt:

$$K_\nu d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt = J_\nu \,.\, d\sigma \,.\, dt \quad . \quad . \tag{335}$$

there is the entropy:

$$L_\nu \,.\, d\nu \,.\, d\sigma \,.\, \cos\theta \,.\, d\Omega \,.\, dt = H_\nu d\sigma \,.\, dt \quad . \quad . \tag{336}$$

which is simultaneously incident on, or emitted by, the surface element.

Similarly, just as we speak of the spatial energy-density of unpolarized radiation uniformly distributed in direction (296) and (297):

$$u = \frac{8\pi}{c}\int K_\nu d\nu \quad . \tag{337}$$

so we can speak of the spatial entropy density of this radiation:

$$s = \frac{8\pi}{c}\int L_\nu d\nu \quad . \tag{338}$$

for which the spectral distribution of the energy can be quite arbitrary.

If we now assume the dependence of the function L_ν on K and ν as known, then the law of normal energy distribution comes out as follows.

We consider unpolarized cavity radiation which is uniform in all directions, has volume V and energy $U = V.u$, and has any spectral distribution of energy whatsoever. Then the normal distribution of energy is that which makes the entropy of the radiation $S = V.s$ a maximum for a constant V and constant U. By (338) the condition for this is:

$$\delta\int_0^\infty L_\nu d\nu = \int_0^\infty \delta L_\nu d\nu = \int_0^\infty \frac{\partial L_\nu}{\partial K}\delta K \,.\, d\nu = 0$$

since ν is not subject to variation ($\delta\nu = 0$). On the other hand, since $\delta U = 0$, we have by (337) also:

$$\delta\int_0^\infty K d\nu = \int_0^\infty \delta K d\nu = 0$$

whereas δK is otherwise quite arbitrary. The last two equations can exist simultaneously only if $\frac{\partial L_\nu}{\partial K}$ is independent of ν and hence can be placed outside the integral sign.

The equation :

$$\frac{\partial L_\nu}{\partial K} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (339)$$

is therefore the necessary and sufficient condition that the entropy should be a maximum, that is, for the normal energy distribution. The physical significance of the constants in (339) is obtained by considering the dependence of the maximum values of the entropy S on the energy U. For when the volume is constant ($\delta V = 0$) we have in general :

$$\delta S = \frac{\delta U}{T}$$

and hence also $\delta s = \frac{\delta u}{T}$, and by (338) and (337), in view of (339) :

$$\frac{\partial L_\nu}{\partial K} = \frac{1}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (340)$$

Since L_ν is assumed to be a known function of K and ν this equation gives us the energy distribution of black body radiation at the temperature T, and hence also the universal function (314). Thus *the central problem of the theory of heat radiation is reduced to the problem of representing the entropy of a linearly polarized beam of monochromatic radiation as a function of the energy and the frequency.* This is the actual path that was followed in originally solving the problem and we shall do the same here.

The equation (340) compels us to ascribe to every single beam of radiation in addition to its entropy a definite temperature T defined by this very equation. The temperature of a beam of radiation is the temperature of a black body which emits the beam in question, and the normal energy distribution is distinguished from all other energy distributions in that all its beams have the same temperature.

The necessity of introducing a radiation temperature as well as a body temperature has also made itself increasingly felt in experimental physics. Thus, since a considerable time ago it has been found useful to speak, not only of the actual temperature of a body but also of an " effective " temperature or a " black body " temperature of the body, that is, of that temperature which the body would need to have if it were black in order to send out the radiation which it actually emits. The " black-body " temperature of a body is no other than the actual temperature of the rays emitted by it. Consequently in general a body has an infinite number of black-body temperatures, namely, a different one for each direction, colour and polarization. The black body temperature is always lower than the actual temperature of the body, because the intensity of a beam emitted by the body is always less than that of a beam emitted by a black body.

§ 111. To find out how the entropy of a beam of radiation depends on its energy and its frequency we use the same method which served earlier, in § 70, for calculating the entropy of a gas mixture. We carry out a reversible adiabatic process with our system, which is here a linearly polarized monochromatic beam. From the second law we then know that the entropy of the beam does not change. Now, if we can arrange the process in such a way that the energy and the frequency change in a known way, we can deduce from this how the entropy of the beam must depend on the energy and the frequency in order that it may remain constant during these changes.

A suitable reversible adiabatic process with the desired properties presents itself to us in the reflection of a beam of radiation from a moving mirror. For, firstly, this process, like all purely mechanical and electrodynamic processes, is reversible (§ 39) and, secondly, the frequency and the energy of the beam are changed by it in a manner which can be specified. Moreover, the velocity of the mirror may be assumed as great as we please. It is sufficient, however, and serves to simplify the calculation, if we assume it to be very small compared with c, the velocity of light.

Let us first calculate the change in the frequency ν caused by the reflection. If we again use the notation and Fig. 1 of IV, § 6, then in the wave function of the incident monochromatic wave the argument is identical with the phase:

$$2\pi\nu\left(t-\frac{x}{c}\right)=2\pi\nu\,.\left(t-\frac{\xi\cos\theta+\eta\sin\theta}{c}\right).$$

In the same way the argument in the wave-function of the reflected wave is the phase:

$$2\pi\nu'\left(t-\frac{x'}{c}\right)=2\pi\nu'\,.\left(t-\frac{-\xi\cos\theta'+\eta\sin\theta'}{c}\right)$$

if here, in contradistinction to our earlier usage (*loc. cit.*), we now take θ' to stand for the *acute* angle of reflection.

Since the electric intensity of field must always vanish everywhere at the reflecting surface, which we may imagine as the bounding surface of an absolute conductor (III, § 92), the electric intensities of both waves must be equal and opposite at all points of this surface and at all times, that is, for all values of η and t; this is possible only if the coefficients of η and t are identical in the arguments of the two wave-functions. If we take the velocity v positive and assume that the mirror moves *towards* the incident radiation (to the left), then in the notation there used we have for the reflecting surface:

$$\xi=-vt+\text{const.}$$

and the two arguments assume the values:

$$\nu\left(t-\frac{-vt\cos\theta+\eta\sin\theta}{c}\right)+\text{const. and}$$

$$\nu'\left(t-\frac{vt\cos\theta'+\eta\sin\theta'}{c}\right)+\text{const.}$$

By identifying the coefficients of t and η we get, since we have assumed $v \ll c$:

$$\nu' = \nu\left(1 + \frac{2v\cos\theta}{c}\right). \tag{341}$$

and:

$$\nu' \sin\theta' = \nu \sin\theta \tag{342}$$

Consequently, also:

$$\sin\theta' = \sin\theta\left(1 - \frac{2v\cos\theta}{c}\right) . \tag{343}$$

and:

$$\cos\theta' = \cos\theta + \frac{2v}{c}\sin^2\theta . \tag{344}$$

We next enquire into the specific intensity K' of the reflected beam and calculate it by applying the first law. Since work is done in moving the mirror against the pressure of the radiation, the energy which is emitted into the vacuum by the mirror during the time dt is greater than the energy of radiation that falls on the mirror in the same time dt by the amount of the work simultaneously performed. The latter is calculated from (335) for a monochromatic linearly polarized beam within the elementary cone $d\Omega$, referred to the element of area $d\sigma$ of the mirror. But this expression holds only for a mirror at rest. When the mirror moves towards the incident radiation, it receives still more energy; and the additional amount is that contained in the space swept out in the time dt by the surface element $d\sigma$, which we may assume arbitrarily great. The size of this space is $d\sigma . v dt$, and, by (291) and (298) the spatial energy-density of the monochromatic linearly polarized radiation in it is:

$$\mathfrak{u}_\nu = \frac{1}{c}\mathbf{K} . d\Omega . \tag{345}$$

Hence the additional amount of energy taken up by the mirror is:

$$\frac{1}{c}\mathbf{K} d\Omega d\nu . d\sigma . v . dt$$

and the total energy incident on the mirror in the time dt is :

$$J_\nu d\sigma dt + \frac{1}{c} K d\Omega \, . \, d\nu \, . \, d\sigma \, . \, v \, . \, dt$$

$$= K \, . \, d\nu \, . \, d\Omega \, . \, d\sigma \, . \, dt \left(\cos\theta + \frac{v}{c}\right) \quad . \quad . \quad (346)$$

In a fully analogous way we can derive the following expression for the energy reflected into the vacuum by the mirror in the time dt for the case where the mirror moves in the direction of the reflected radiation and consequently causes less energy to be received than when it is at rest :

$$K' \, . \, d\nu' \, . \, d\Omega' \, . \, d\sigma \, . \, dt \left(\cos\theta' - \frac{v}{c}\right) \quad . \quad . \quad (347)$$

On the other hand, the work performed against the radiation by the mirror in the time dt is :

$$v \, . \, dt \, . \, d\sigma \, . \, p \quad . \quad . \quad . \quad . \quad . \quad (348)$$

In this expression the pressure of radiation p is composed of the pressures of the incident and the reflected linearly polarized beams. Hence by (321) :

$$p = \frac{J_\nu \cos\theta}{c} + \frac{J'_{\nu'} \cos\theta'}{c} \quad . \quad . \quad (349)$$

Here we may, without introducing an appreciable error, use for J_ν and $J'_{\nu'}$ the formula (335) for a surface at rest, because the correction to be applied to the work term (348) owing to the motion of the mirror, as expressed in the factor v, would be of lower order of magnitude than the first. We may even treat the two summands of (349) as equally great, but we refrain from this in order to maintain the symmetry between the incident and the reflected radiation.

If, according to the first law, we set the difference of the expressions (347) and (346) equal to the expression (348), inserting the value for the pressure from (349), we get the equation :

$$K'd\nu'd\Omega'\left(\cos\theta' - \frac{v}{c}\right) - Kd\nu d\Omega\left(\cos\theta + \frac{v}{c}\right) = \frac{v}{c}\left(J_\nu \cos\theta + J'_{\nu'} \cos\theta'\right)$$

or, substituting the values of J_ν and $J'_{\nu'}$ from (335) :

$$\frac{K'd\nu'd\Omega'\left(\cos\theta' - \frac{v}{c} - \frac{v}{c}\cos^2\theta'\right)}{Kd\nu d\Omega\left(\cos\theta + \frac{v}{c} + \frac{v}{c}\cos^2\theta\right)} = 1 \ . \qquad (350)$$

This equation gives the desired relationship between the specific intensities K' and K of the reflected and the incident radiation. To evaluate it we must introduce the relations worked out above between the frequencies and the directions of the two beams. As regards the ratio of the differential expressions :

$$\frac{d\nu'd\Omega'}{d\nu d\Omega} = \frac{d\nu' \, . \sin\theta' \, . \, d\theta'}{d\nu \, . \sin\theta \, . \, d\theta}$$

we must bear in mind that ν and θ are independent of one another, so that this ratio is expressed by the functional determinant of the transformation :

$$\frac{\sin\theta'}{\sin\theta} \cdot \begin{vmatrix} \frac{\partial\nu'}{\partial\nu} & \frac{\partial\nu'}{\partial\theta} \\ \frac{\partial\theta'}{\partial\nu} & \frac{\partial\theta'}{\partial\theta} \end{vmatrix} = \frac{\sin\theta'}{\sin\theta}\left(\frac{\partial\nu'}{\partial\nu}\right)_\theta \cdot \left(\frac{\partial\theta'}{\partial\theta}\right)_\nu$$

since, by (343), $\frac{\partial\theta'}{\partial\nu} = 0$.

If we use the relations (341) and (343) this gives us the desired value :

$$\frac{d\nu'd\Omega'}{d\nu d\Omega} = 1 - \frac{2v}{c}\cos\theta = \frac{\nu}{\nu'} \quad . \quad . \quad . \quad (351)$$

Further, by (344) and (341) we have :

$$\frac{\cos\theta' - \frac{v}{c} - \frac{v}{c}\cos^2\theta'}{\cos\theta + \frac{v}{c} + \frac{v}{c}\cos^2\theta} = 1 - \frac{4v}{c}\cos\theta = \frac{\nu^2}{\nu'^2}\,. \qquad (352)$$

Hence equation (350) runs :

$$\frac{K'}{K}\cdot\frac{\nu^3}{\nu'^3} = 1$$

or :

$$\frac{K'}{\nu'^3} = \frac{K}{\nu^3} \qquad . \qquad . \quad . \quad . \qquad (353)$$

That is, *when a monochromatic beam of radiation is reflected by a moving mirror the specific intensity of the energy radiation increases proportionally to the cube of the frequency.*

We now pass on to calculate the specific intensity $\boldsymbol{L}'$ of the entropy radiation in the reflected beam. This is essentially easier because according to the second law, since the process is reversible and adiabatic, the entropy of the reflected beam is the same as that of the incident beam. In other respects the discussion runs along exactly analogous lines to that used for the energy in the preceding section, so that, corresponding to the relation (350) for the first law, we here obtain as the relation for the second law :

$$\frac{\boldsymbol{L}'d\nu'd\Omega'\left(\cos\theta' - \frac{v}{c}\right)}{\boldsymbol{L}d\nu d\Omega\left(\cos\theta + \frac{v}{c}\right)} = 1 \quad . \qquad . \quad (354)$$

Consequently, since by (344) and (341) :

$$\frac{\cos\theta' - \frac{v}{c}}{\cos\theta + \frac{v}{c}} = 1 - \frac{2v}{c}\cos\theta = \frac{\nu}{\nu'},$$

we get :

$$\frac{\boldsymbol{L}'}{\boldsymbol{L}}\cdot\frac{\nu^2}{\nu'^2} = 1$$

or :

$$\frac{L'}{\nu'^2} = \frac{L}{\nu^2} \quad . \quad . \quad . \quad . \qquad (355)$$

That is, *when a monochromatic beam of radiation is reflected by a moving mirror the specific intensity of the entropy radiation increases proportionally to the square of the frequency.*

§ 112. The above results enable us to follow out the train of ideas described in § 111. We know that L is a perfectly definite function of the independent variables K and ν and we know further that for reflection at a plane mirror $\frac{K}{\nu^3}$ and also $\frac{L}{\nu^2}$ remain invariant. Hence it necessarily follows that the quantity $\frac{L}{\nu^2}$ can depend only on $\frac{K}{\nu^3}$ and not on a second variable, such as ν; for in that case $\frac{L}{\nu^2}$ would have to change during the reflection, since ν changes. Hence we have :

$$L = \nu^2 . f\left(\frac{K}{\nu^3}\right) \quad . \quad . \quad . \qquad (356)$$

where f denotes a certain function of a single argument. The equation (356) expresses *Wien's Displacement Law.* Its importance lies in the fact that it reduces the function L which is dependent on two variables to a function of a single variable.

Wien's Displacement Law may be formulated in many different ways and is capable of being applied in correspondingly different ways which can in part be subjected to experimental tests.

Firstly, it follows from (340) that :

$$\frac{1}{T} = \frac{\partial L}{\partial K} = \frac{1}{\nu} \cdot \dot{f}\left(\frac{K}{\nu^3}\right)$$

where the dot over f denotes differentiation with respect to the argument; or, conversely, in terms of K :

$$K = \nu^3 . g\left(\frac{\nu}{T}\right) \quad . \quad . \quad . \quad . \quad . \qquad (357)$$

where g again denotes a certain function of a single argument.

All these equations hold for radiation in a vacuum. But we can immediately make them independent of the nature of the medium traversed by introducing the universal function (314). For if we substitute in the left-hand side of equation (314) the values that refer to a vacuum, we get for the expression of the universal function:

$$F(\nu, T) = c^2\nu^3 \cdot g\left(\frac{\nu}{T}\right) \cdot \qquad \cdot \qquad (358)$$

Hence $c^2 \cdot g\left(\frac{\nu}{T}\right)$ is also a universal function ϕ of ν and T and we obtain, no matter what medium is traversed by the radiation :

$$K_\nu = \frac{\nu^3}{q^2} \cdot \phi\left(\frac{\nu}{T}\right) \qquad (359)$$

as the expression of Wien's Displacement Law, which relates the specific intensity of the energy radiation to the frequency, temperature and velocity of propagation in any arbitrary medium. If we again choose a vacuum then the relation becomes :

$$K_\nu = \frac{\nu^3}{c^2} \cdot \phi\left(\frac{\nu}{T}\right) \qquad (360)$$

§ 113. In black body radiation all the beams have the same temperature T, and their intensities are independent of their direction. Then, by (297), the spatial energy-density of unpolarized monochromatic radiation in a vacuum is :

$$u_\nu = \frac{8\pi\nu^3}{c^3} \cdot \phi\left(\frac{\nu}{T}\right) \quad \cdot \qquad (361)$$

and the total spatial energy-density is :

$$u = \int_0^\infty u_\nu d\nu = \frac{8\pi}{c^3}\int_0^\infty \nu^3\phi\left(\frac{\nu}{T}\right)d\nu \qquad (362)$$

If we transform from the variable ν to the variable $\frac{\nu}{T} = x$, the expression becomes:

$$u = \frac{8\pi T^4}{c^3} \int_0^\infty x^3 \phi(x) dx$$

Since the integral here has a constant value, this equation represents the Stefan–Boltzmann law (326).

The expressions (360) and (361) contain all that Wien's Displacement Law has to say about the energy distribution in the normal spectrum. According to this it is only necessary to know the energy distribution for a single definite temperature T in order to be able to determine the dependence of the function ϕ on its argument and hence also the energy distribution for every other temperature. Since $\mathfrak{K}_\nu$ and $\mathfrak{u}_\nu$ vanish both for $\nu = 0$ and $\nu = \infty$—in the latter case because the integral (362) has a finite value—these quantities have a maximum for a certain value of ν, and so Wien's law gives us information about the way in which the maximum depends on the temperature and also its magnitude.

§ 114. In experimental physics it is usual to characterize monochromatic radiation not by the frequency ν but by the wave-length $\lambda = \frac{c}{\nu}$ which is directly measurable. Similarly we set the specific intensity of radiation not equal to $\mathfrak{K}_\nu$ but to E_λ; moreover E_λ is not equal to $\mathfrak{K}_\nu$, but rather:

$$E_\lambda \cdot d\lambda = \mathfrak{K}_\nu \cdot d\nu = \mathfrak{K}_\nu \cdot \frac{c}{\lambda^2} d\lambda \qquad (363)$$

Hence by (360):

$$E_\lambda = \frac{c^2}{\lambda^5} \phi\left(\frac{c}{\lambda T}\right) \quad . \qquad (364)$$

It is to be particularly noted that the maximum of E_λ lies at a different point of the spectrum and has a different value from the maximum of $\mathfrak{K}_\nu$. The maximum of E_λ is obtained from the equation:

$$\frac{dE_\lambda}{d\lambda} = 0$$

or by (364):

$$\phi\left(\frac{c}{\lambda T}\right) + \frac{c}{5\lambda T}\dot{\phi}\left(\frac{c}{\lambda T}\right) = 0$$

This equation gives a perfectly definite universal value for the argument $\frac{c}{\lambda T}$, so that *in vacuo* the following relation holds for the wave-length λ_m of the maximum of the intensity of radiation E_λ at the temperature T:

$$\lambda_m T = b \quad . \quad . \quad . \quad . \quad . \quad . \quad (365)$$

The numerical value of b has been measured, the result being:

$$b = 0{\cdot}290 \text{ [cm. degree]} \quad . \quad . \quad . \quad (366)$$

The value of the maximum of the radiation in the spectrum is obtained from (364) by writing in it $\lambda = \lambda_m$. Then, on account of (365), we have:

$$E_{\max} = \text{const.}\, T^5 \quad . \quad . \quad . \quad . \quad (367)$$

All these consequences of Wien's Displacement Law have been confirmed as accurately as we may well expect by many measurements. On the other hand this law leaves the important question of the dependence of the universal function ϕ on its argument entirely untouched. This is, as a matter of fact, a problem which cannot be successfully dealt with by the classical theory and which, on this account, has dealt it a fatal blow. Its solution can be found only by taking a fundamentally new step on the road to discovering the nature of entropy.

PART FOUR

ATOMIC THEORY. THE THEORY OF QUANTA

CHAPTER I

THE MACROSCOPIC AND THE MICROSCOPIC VIEW

FLUCTUATIONS

§ 115. ALL our previous discussions have been founded on assumptions which we could regard as valid without restriction both as regards range and content, namely on the fundamental principles of mechanics and electrodynamics as well as on the two principal laws of heat theory. This constitutes the strength but also the weakness of our deductions. Their strength consists in the fact that the theorems we have deduced hold in all cases with absolute accuracy, and their weakness is that these results for the most part are rather general in character and so leave a number of interesting special questions unanswered. Thus we were able to reduce the whole thermodynamic behaviour of a substance to a single characteristic function (§ 54 to § 56) of the independent variables involved. But our discussion taught us nothing at all of the form of this function. The same holds of the laws of heat radiation (§ 114).

Hence, if we wish to make progress in unravelling the laws underlying thermal phenomena, we must first fix our attention on the nature of the characteristic function by which all thermodynamic properties of the system are conditioned, namely on the nature of entropy. Our task will consist in endeavouring to grasp the significance of this quantity from the mechanical and the electrodynamic point of view. That this is not a simple task is obvious. For the remarkable property of entropy in virtue of which it changes only uni-directionally with the time stands in opposition to all mechanical and electrodynamic laws, in which the sign of the time factor plays no part. We can make progress here only by introducing a special idea entirely new in principle, an idea which was first introduced into science for a definite purpose and with conscious intention by L. Boltzmann.

A hint of the direction in which we have to strike out is furnished by the train of ideas used in deriving the second law. To give ourselves a clearer view we there (§ 39) assigned to every given state of a physical system a certain "thermodynamic probability" or a certain "thermodynamic weight" in a certain sense, and we found quite generally (§ 47) that the entropy of the system is a measure of this thermodynamic probability. The question which we now propose to deal with is this: how is it possible to explain from the point of view of mechanics and electrodynamics that different states of a system have different thermodynamic weights?

An answer to this question is possible only by first obtaining a closer insight into the nature of physical systems. To accomplish this it is necessary to introduce a higher order of refinement into our considerations. Hence, besides the point of view hitherto used, which was founded on thermal measurements and which we shall call the macroscopic view, we shall make use of a finer, microscopic, point of view of which we assume that it will force itself upon us whenever we wish to analyse the physical system in question in far greater detail than has hitherto been done. In the macroscopic view the state of a system is determined by its temperature, its density, the number of moles of all kinds, the intensities of radiation in all directions, colours and states of polarization. In the microscopic view all these quantities disappear as self-dependent concepts; the only meaning they retain is that of quantities denoting certain mean values. The homogeneity of a body resolves itself into an irregular hurly-burly of an immense number of extremely small electrically charged particles moving with great speed among themselves; in place of the moles, whose weight is standardized by convention (§ 16), we now have perfectly definite *molecules*; in place of a heat ray of definite intensity we have an *electromagnetic wave* with an intensity which varies in a definite way with the time. The importance of the microscopic point of view, according to this, consists primarily in the fact that, by adopting it, we deprive heat entirely of its position as an independent concept and apparently reduce it to mechanical and electrodynamic concepts, or, as we may briefly say, to dynamic concepts. This signifies a fundamental step forwards in unifying the physical picture of the world. Henceforth heat forms a part of dynamics, and so all the laws that hold in the latter will now also come into force for the former.

§ 116. However revolutionary in principle the introduction of the dynamical or microscopic point of view may be in the theory of heat, it seems at first sight to be of no practical advantage and doubts even arise as to whether it is permissible.

For in dynamics the course of every event in time is uniquely determined according to well-known laws by the initial state of the system under consideration. That is the most that can be expected of any theory. But when applied to thermal phenomena this direct method fails completely for the microscopic point of view because the initial state of a thermal system is never known in the microscopic sense. All that we can control, that is, measure, are only macroscopic quantities, and there are far too few of them to allow the corresponding microscopic quantities to be deduced. We can only say that for a particular value of a macroscopic quantity, for example, the density or the intensity of radiation, there is an enormous number of values of the corresponding microscopic quantities, namely the positions of the individual molecules or the field intensities of the electromagnetic waves which are compatible with the given value of the macroscopic quantity. Or, expressing this more shortly and more generally, we may say that a definite macroscopic state of a system admits of an enormous number of microscopic states. And, since the course of the event in time depends on the initial state, it will by no means be determined by the macroscopic state, since very many different events may follow from a given macroscopic state. We might, therefore, easily be led to surmise that the progress promised by the dynamic view is illusory. For apart from the fact that we can neither calculate nor experimentally control microscopic events we are even compelled to expect that an initial state which is defined macroscopically with absolute precision is not of necessity followed by another definite macroscopic event—and this is in striking contradiction to all our experimental knowledge.

To arrive at definite and precise results in spite of the uncertainty mentioned we make use of the following expedient. We eliminate the uncertainty which is contained in the fact that a very great number of microscopic states belong to a given macroscopic state by allowing the event to be repeated very many times, namely, by starting out always from the same macroscopic state of the system and investigating how the event takes place each time. We shall then obtain many different events, depending on the kind and the number of different microscopic states possible under the assumed conditions. But if we now form the mean of all these results we may hope to arrive at perfectly definite laws. These laws will then have only a statistical or probability character, but they can be formulated no less exactly than any other law of dynamics. A simple example of a statistical law, which claims to be absolutely accurate, will illustrate this. If an ordinary die, symmetrically constructed as a cube, is thrown only once, the throw is fully indeterminate. But if we repeat the throw sufficiently often and take the average by dividing the total number of points ("spots") thrown by the number of throws, we get the result 3·5 to any degree of accuracy.

We see that in this case too we are dealing with a strict law, but one of a totally different kind from those of dynamics. We may therefore call it a statistical law and contrast it with dynamical laws. Statistical laws deal not with individual cases but only with mean values. And whereas in the domain of the microscopic view, that is, in mechanics and electrodynamics, the dynamical laws hold sway, the macroscopic view and with it the whole theory of heat leads to statistical or probability laws. We see immediately that the practical importance of these statistical laws must not be rated lower than that of dynamical laws if we consider that a physicist never performs an experiment once but always repeats it several times and often a very great number of times.

§ 117. By introducing the microscopic point of view we are enabled to answer the question as to the nature of entropy and to examine more closely the concept of thermodynamic probability. It does not, indeed, give us a direct answer to the question; for this we further require a special hypothesis. But it furnishes us with a frame within which such a hypothesis can find a place. For it now suggests itself to us very simply and naturally to bring the thermodynamic probability of a state which is defined by macroscopic thermal data into relationship with the number of microscopic states compatible with this state. In dynamics the concept of probability plays no part or, as we may say, *all microscopic states are equally probable in dynamics.* Since the probability of a result is given quite generally by the number of equally probable states that produce the result, it suggests itself to us to define the probability of a macroscopic state by means of the number of microscopic states that belong to it. In so-called classical theory the question as to what is meant when we speak of a definite number of microscopic states as belonging to a definite macroscopic state can be answered in only a restricted and relative sense. For in classical theory the totality of microscopic states forms a continuum, a continuously extended manifold.

In view of this we shall immediately express the hypothesis in its most definite and most far-reaching form, a form which goes considerably beyond the classical theory and has shown itself to be superior in competition with it. It runs: *the totality of microscopic states forms a discrete manifold. Every macroscopic state of a physical system comprises a perfectly definite number of microscopic states of the system, and this number represents the thermodynamic probability or the statistical weight G of the macroscopic state.* It is a measure of the entropy S of the system in the corresponding macroscopic state, thus:

$$S = f(G) \quad . \quad . \quad . \quad . \quad . \quad (368)$$

where f denotes a universal function of a single argument.

One objection against this relationship suggests itself at once, namely that the entropy S is continuously variable whereas the statistical weight G, being a whole number, varies discontinuously. This difficulty can be overcome only by assuming G to be enormously great, so great that a change of one unit in G influences f to only a vanishingly small degree. This condition of course fundamentally limits the region in which the macroscopic thermodynamical point of view is applicable. If the number of microscopic variables is so small that only a moderately large number results for the statistical weight G, thermodynamics loses its meaning. But this agrees perfectly with what we found earlier, namely that we can speak neither in the case of absolutely plane waves (§ 95) nor in that of absolutely monochromatic waves (§ 97) of a finite specific intensity of radiation nor, therefore, of a finite temperature of the radiation; no more than we can speak of a temperature or entropy when we have only a few molecules. We cannot, however, fix a definite minimum value for G or a definite limit within which the thermodynamic point of view ceases to hold. We can only say that the relations that follow from (368) hold the more accurately the greater the value of G. In all our future considerations we shall assume G to be sufficiently great so that we can treat it as a continuously variable quantity.

§ 118. The form of the universal function f in (368) comes out directly if we consider how, in the case of two mutually independent systems (1) and (2), the entropy on the one hand and the statistical weight of the total system (12) on the other are built up from the properties of the individual systems. For in the first place we have, by § 47 :

$$S_{12} = S_1 + S_2 \quad . \quad . \quad . \quad . \quad (369)$$

Secondly, since every microscopic state of the one system can be combined with every microscopic state of the other system :

$$G_{12} = G_1 . G_2 \quad . \quad . \quad . \quad . \quad . \quad (370)$$

If we now write the relation (368) both for the total system (12) as well as for each of the separate systems (1) and (2), and substitute the values for S_{12}, S_1 and S_2 in (369), we get, taking into account (370) :

$$f(G_1G_2) = f(G_1) + f(G_2) \quad . \quad . \quad . \quad (371)$$

Differentiating with respect to G_1 we get :

$$G_2\dot{f}(G_1G_2) = \dot{f}(G_1)$$

and differentiating, further, with respect to G_2 :

$$\dot{f}(G_1G_2) + G_1G_2\ddot{f}(G_1G_2) = 0$$

or :

$$\dot{f}(G) + G\ddot{f}(G) = 0.$$

The general integral of this differential equation of the second order is :

$$f(G) = k \log G + k'$$

Hence, by (371) :

$$k' = 0$$

and by (368) :

$$S = k \log G \quad . \quad . \quad . \quad . \quad (372)$$

which expresses the entropy quite generally in terms only of the statistical weight or the thermodynamic probability.

The logarithmic relationship between entropy and probability was first disclosed by L. Boltzmann. But the equation (372) differs in two essential points from that of Boltzmann.

Firstly the universal factor k is missing in Boltzmann's expression; this is because Boltzmann never calculated with molecules but only with moles and it therefore never occurred to him to introduce such a factor. Secondly, and this is a much more significant point, in Boltzmann's classical statistics a factor of proportionality remains completely indefinite in the value of the quantity here denoted by G: this causes the value of the entropy to contain an undetermined additive constant. For Boltzmann regarded the counting up of the microscopic states belonging to a definite macroscopic state only as an arithmetical device of a certain arbitrary character.

In contrast with this the value of the entropy here has, according to (372) a perfectly definite, absolute, and, indeed, positive value. This is a theorem of fundamental importance which goes beyond the classical theory. From it we obtain, as will be shown, the law of energy distribution in the normal spectrum for radiant heat and also Nernst's Heat Theorem for the heat content in bodies: both these consequences are foreign to the classical theory. Comparison with experimental measurements then also yields the numerical value of the constant k. At the present point we can state only the order of magnitude of k. For since G is enormously great (§ 117) and S has moderate values in the usual units, k, measured in calories and degrees centigrade, will have a very small value.

§ 119. Although the fundamental relation (372) furnishes a method of expressing the whole thermodynamic behaviour of a system in terms of its microscopic structure we have not yet, of course, solved the problem by merely establishing the relation. For we have yet to calculate the number G for any case that may present itself; this problem has been solved completely for only a few systems of simple type. But before we proceed to the applications we shall make a few remarks on the physical meaning of the whole theory, which will lead to remarkable consequences and will at the same time furnish the means of testing the validity of the theory experimentally.

The starting point of our discussion was the statement (§ 117) that all microscopic states are equally probable. If we enquire into the physical meaning of this statement the only possible reply surely appears to be this: the probability of finding a physical system, which is subject to definite fixed macroscopic conditions, in a definite microscopic state at any time, is equally great for all the microscopic states possible under the given conditions. From this it necessarily follows that in the course of time the system really passes through *all* the microscopic states corresponding to its macroscopic conditions. If, for example, we have a body enclosed in an envelope impermeable to heat, it will in the course of time assume all the microscopic states that are possible at constant volume and for a constant value of the energy. This is usually known as the "ergodic hypothesis" (*Ergodenhypothese*).

At first sight this appears to be an amazing and unacceptable statement. For the microscopic states in the case in question include not only those corresponding to the macroscopic thermodynamic state of equilibrium but also those which belong to all the other macroscopic states, provided only that the volume and the energy are the same. In other words, the body exhibits a behaviour totally in disagreement with the thermodynamic laws. There is no question of the state of equilibrium being in any sense a state of rest. Even if the body should once find itself in a state of uniform density and uniform temperature it will subsequently change this state of itself; differences of density and temperature will arise spontaneously, to such an extent, in fact, that ultimately *every* possible deviation from thermodynamic equilibrium will be realized as often as we like. This appears to contradict flatly the demands of the second law.

Nevertheless this contradiction can be disposed of. For quantitative tests will not only show that it is groundless but will also lead further to positive deductions which are directly confirmed by experiment and, therefore, lend valuable support to the theory.

If thermodynamic equilibrium is not a static but a statistical equilibrium about which fluctuations of every kind occur we are led to enquire particularly to what extent and how often these fluctuations occur. An answer to this is clearly given by the theorem that the mathematical probability for the occurrence of any macroscopic state is represented by a fraction, whose numerator is the statistical weight G of the macroscopic state and whose denominator is the sum of the statistical weights of all the macroscopic states that are at all possible under the given conditions. The probability is greatest for the state of thermodynamic equilibrium, since maximum entropy corresponds to it. Let its statistical weight be G_m. Then the ratio of the probability of any state to the probability of the equilibrium state is as G is to G_m; and this quotient gives a quantitative measure for the frequency of occurrence of the corresponding deviation from equilibrium. Using (372) we obtain for its values :

$$\frac{G}{G_m} = e^{\frac{S - S_m}{k}}$$

where S_m denotes the maximum value of the entropy. If we set :

$$S - S_m = \Delta S. \quad . \quad . \quad . \qquad (373)$$

then ΔS is negative, and we get :

$$\frac{G}{G_m} = e^{\frac{\Delta S}{k}} \quad . \quad . \quad . \quad . \qquad (374)$$

This is a proper fraction, as it should be. This relation allows us to calculate the relative frequency with which each deviation from equilibrium occurs. Now we have seen that the constant k has a very small value, hence for a moderate value of ΔS the quotient (374) will come out extremely small, that is, an appreciable deviation from equilibrium is extremely rare. If the deviation is to occur more frequently then ΔS must be of the order of magnitude of k, that is, the fluctuations about the state of thermodynamic equilibrium must have an exceedingly small amplitude.

§ 120. Let us carry our argument a little further by treating a specially simple case, say that of an ideal gas. Let the number of moles n, the energy U and the volume V be given. Then in the state of equilibrium the gas has uniform density and uniform temperature throughout its volume. Let us now consider a part of the gas containing n_1 moles which has the energy $U_1 = \frac{n_1 U}{n}$ and the volume $V_1 = \frac{n_1 V}{n}$ in the state of equilibrium and let us enquire into the frequency with which small deviations ΔU_1 and ΔV_1 from the normal values occur. Since the total energy U and the total volume V of the gas remain constant, we have:

$$\left.\begin{aligned} \Delta U_1 + \Delta U_2 &= 0 \\ \Delta V_1 + \Delta V_2 &= 0 \end{aligned}\right\}. \tag{375}$$

where the number of the remaining moles is n_2, their energy U_2 and their volume V_2. Also, the change of entropy:

$$S = S_1 + S_2$$

corresponding to the fluctuation will be, if we disregard vanishingly small terms:

$$\begin{aligned}
\Delta S &= \Delta S_1 + \Delta S_2 \\
&= \left(\frac{\partial S}{\partial U}\right)_1 \Delta U_1 + \left(\frac{\partial S}{\partial V}\right)_1 \Delta V_1 + \frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_1 \Delta U_1^2 \\
&\qquad + \left(\frac{\partial^2 S}{\partial U \partial V}\right)_1 \Delta U_1 \Delta V_1 + \frac{1}{2}\left(\frac{\partial^2 S}{\partial V^2}\right)_1 \Delta V_1^2 \\
&+ \left(\frac{\partial S}{\partial U}\right)_2 \Delta U_2 + \left(\frac{\partial S}{\partial V}\right)_2 \Delta V_2 + \frac{1}{2}\left(\frac{\partial^2 S}{\partial U^2}\right)_2 \Delta U_2^2 \\
&\qquad + \left(\frac{\partial^2 S}{\partial U \partial V}\right)_2 \Delta U_2 \Delta V_2 + \frac{1}{2}\left(\frac{\partial^2 S}{\partial V^2}\right)_2 \Delta V_2^2
\end{aligned}$$

where the bracketed quantities all refer to the state of equilibrium.

If we now apply the known relations :

$$\frac{\partial S}{\partial U}=\frac{1}{T},\quad \frac{\partial S}{\partial V}=\frac{p}{T}=\frac{Rn}{V},\qquad U=nc_vT+\text{const.}$$

and also take (375) into account, the last equation simplifies to :

$$\Delta S=-\frac{1}{2c_vT^2}\left(\frac{1}{n_1}+\frac{1}{n_2}\right)\Delta U_1{}^2-\frac{R(n_1+n_2)^2}{2V^2}\left(\frac{1}{n_1}+\frac{1}{n_2}\right)\Delta V_1{}^2$$

If, further, we assume n_2 to be great compared with n_1 the terms in $\frac{1}{n_2}$ vanish, and introducing the molar volume $v=\frac{V}{n_1+n_2}$ and omitting the index 1, we obtain :

$$\Delta S=-\frac{\Delta U^2}{2c_vT^2n}-\frac{R\Delta V^2}{2v^2n}\quad .\quad .\quad .\quad (376)$$

If we substitute this value in (374) we have the probability that an ideal gas in thermal equilibrium, consisting of n moles at the temperature T and molar volume v and forming part of a much greater quantity of gas, deviates by the amounts ΔU and ΔV from the normal values of the energy and volume. Or in other words, the fluctuations of the energy and the volume about the values for thermodynamic equilibrium for such a gas are of the order of magnitude :

$$\Delta U=\sqrt{2c_vT^2nk}\quad .\quad .\quad (377)$$

$$\Delta V=\sqrt{\frac{2v^2nk}{R}}\quad .\quad .\quad (378)$$

Since, as we shall see later (§ 141), the universal constant k when given in ergs is of the order 10^{-16} and hence of the order 10^{-23} in calories, the fluctuations ΔU and ΔV ordinarily have extremely small values.

But we can go a step further. If by integrating the exponential function (374) with respect to ΔU and ΔV between infinitely great positive and negative values of these variables we form the sum of the probabilities of all the deviations from the values in the equilibrium state taken together we again obtain in general a small value; that is, the probability for *any* deviation from the equilibrium state is appreciable, under ordinary circumstances, only for very small deviations, or *the statistical weight of the state of thermodynamic equilibrium is very great compared with the statistical weight of all the possible states taken together*.

It is clear from this statement that under ordinary circumstances every kind of fluctuations about this state of thermodynamic equilibrium are quite inaccessible to measurement. The position is different, however, in extreme cases. At high temperatures T and when the volume v of the moles is very great, that is, when the dilution is great, the fluctuations must become appreciable; if, however, the number n of moles increases then, although the fluctuations of the energy U and of the volume V increase, the fluctuations of the energy u referred to a mole and of the volume v of a mole decrease. Various experimental methods have been devised to produce the actual conditions under which the deviations of a physical system from the state of equilibrium can be made manifest; in each case the fluctuations have been found to be of the amount calculated. Hence the important result follows that the statistical theory of thermodynamic equilibrium is not only compatible with experimental results but is indeed demanded by it.

§ 121. It is obvious that in the light of the point of view here developed the second law of thermodynamics acquires a fundamentally different character. The entropy of a physical system completely isolated from its surroundings can also decrease and will, indeed, decrease if we wait long enough. But what then remains of the second law? Its physical meaning is that any given state of a system is followed by a still more probable state or a state of still greater statistical weight—*not*, it is true, of necessity, but still, in *most* cases. As we have already seen in § 116 we can escape from the unsatisfactory feature contained in this mode of formulation by adding the words " in the mean." With this qualification, which is of no importance whatsoever in ordinary practice and which does justice to the actual facts, the law of the increase of entropy again holds with absolute accuracy.

CHAPTER II

GROUP OF SIMILAR SYSTEMS. SUM OF STATES. DEGENERATE SYSTEMS

§ 122. A CALCULATION of the entropy of a physical system can be effected on the basis of equation (372) for the case when the system consists of a group of systems entirely alike but completely isolated from one another; we shall call each of the component systems an "elementary system." For in this case we can directly specify the statistical weight G of a definite macroscopic state. According to our assumption (§ 117) each of these elementary systems which we regard, for example, as a kind of oscillators, can have discrete series of states, whose energies (positive) we shall denote in their order of magnitude as:

$$\epsilon_0 < \epsilon_1 < \epsilon_2 < \ . \ . \ . \ < \epsilon_n < \epsilon_{n+1} < \ . \ . \ .$$

Just as a definite amount of energy corresponds to each individual state let a definite state correspond to each individual amount of energy. Suppose N such elementary systems are present in all. Let us fix our attention on a definite macroscopic state of the system having an amount of energy E and let this state be characterized by the number of elementary systems which have each a definite energy, or, as we may say, by the way in which the total energy E is distributed over the individual elementary systems. If we denote the number of elementary systems that have the energy ϵ_n by N_n then the numbers N_0, N_1, N_2 . . . N_n . . ., represent the way in which the energy has been distributed or the law of distribution of the energy. Let this law define the macroscopic state of the total system. The following relations then hold :

$$N_0 + N_1 + N_2 + \ldots = N \quad . \quad . \qquad (379)$$

$$N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \ldots = E \; . \quad . \qquad (380)$$

We next enquire into the statistical weight G of a definite macroscopic state which is to be regarded as given, that is, into the number of microscopic states of the total system which are possible for the distribution law given by the numbers N_0, N_1, N_2. . . . In general a macroscopic state will comprise very many microscopic states. For, knowing the number of elementary systems which have a definite energy ϵ_n does not mean that we also know *which* systems have this energy. Rather, if we exchange the energies of any two elementary systems we get a new allowable microscopic state for each exchange. We can obtain a concrete picture of a definite microscopic state by means of an array of figures thus : number the elementary systems from 1 to N, write these numbers in a row and write below each number the amount of energy which the corresponding elementary system has in the microscopic state in question. Thus for $N =$ 10, that is, ten elementary systems :

$$\begin{array}{cccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ \epsilon_4 & \epsilon_0 & \epsilon_2 & \epsilon_0 & \epsilon_2 & \epsilon_2 & \epsilon_4 & \epsilon_3 & \epsilon_1 & \epsilon_2 \end{array}$$

This microscopic state belongs to the macroscopic state which is characterized by the law of distribution of energy :

$$N_0 = 2,\ N_1 = 1,\ N_2 = 4,\ N_3 = 1,\ N_4 = 2.$$

But the same macroscopic state still contains many other microscopic states, namely just as many as there are permutations of these quantities in the second row. All together these come to :

$$\frac{10!}{2!\,1!\,4!\,1!\,2!} = 37800$$

microscopic states.

By generalizing this calculation appropriately we get immediately for the desired statistical weight of the given macroscopic state :

$$G = \frac{N\,!}{N_0\,!\,N_1\,!\,N_2\,!\,\ldots\,N_n\,!\,\ldots} \quad . \quad . \qquad (381)$$

§ 123. We shall assume now and everywhere in the sequel that the number of elementary systems N is enormously great, so great, indeed, that not only the N in the numerator of the expression (381) but also the great majority of the N_n's in the denominator have a very great value. Without introducing an appreciable error we can then neglect those factors in the denominator, in which N_n are smaller numbers and we then have to do only with the terms formed of large N_n's. This assumption gives us the mathematical advantage that we can regard the N_n's as continuously variable, since a change of one unit in a large number is vanishingly small compared with the number itself. Formally the factorial N although actually an integer can be replaced by a continuous function of N. For this purpose we first take the logarithm :

$$\log N\,! = \sum_{n=1}^{n=N} \log n = \sum_{1}^{N} \log n \,.\, \Delta n$$

In the sum on the right the terms with rather small values of n play only a subordinate part; and in the terms with the greater values for n we may replace Δn by dn. Hence we have :

$$\log N\,! = \int_1^N \log n \,.\, dn + \;.\;.\;.$$

So :

$$\log N\,! = N \log \frac{N}{e} + \;.\;.\;.$$

The dots are to indicate a small correction term. Accordingly we may write :

$$N\,! = \left(\frac{N}{e}\right)^N .\, f(N) \quad . \qquad (382)$$

where $f(N)$ is now at any rate of a lower order of magnitude than the power term preceding it. We shall calculate $f(N)$ only for the limit $N \longrightarrow \infty$. To do this we start out from the infinite product:

$$\sin x = x \cdot \left(1 - \frac{x}{\pi}\right)\left(1 + \frac{x}{\pi}\right)\left(1 - \frac{x}{2\pi}\right)\left(1 + \frac{x}{2\pi}\right) \cdots \quad (383)$$

And for $x = \frac{\pi}{2}$:

$$1 = \frac{\pi}{2}\left(1 - \frac{1}{2}\right)\left(1 + \frac{1}{2}\right)\left(1 - \frac{1}{4}\right)\left(1 + \frac{1}{4}\right) \cdots$$

or:

$$1 = \frac{\pi}{2} \cdot \frac{1 \cdot 3}{2 \cdot 2} \cdot \frac{3 \cdot 5}{4 \cdot 4} \cdot \frac{5 \cdot 7}{6 \cdot 6} \cdots$$

This is known as Wallis's equation and may be written in the form:

$$\operatorname*{Lim.}_{N=\infty} \frac{2 \cdot 2}{1 \cdot 3} \cdot \frac{4 \cdot 4}{3 \cdot 5} \cdots \frac{2N \cdot 2N}{(2N-1)(2N+1)} = \frac{\pi}{2}. \quad (384)$$

or:

$$\text{Lim.} \frac{2 \cdot 4 \cdot 6 \cdot \ldots \cdot 2N}{1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2N-1)} \cdot \frac{1}{\sqrt{2N+1}} = \sqrt{\frac{\pi}{2}}$$

or:

$$\text{Lim.} \frac{(2 \cdot 4 \cdot 6 \cdot \ldots \cdot 2N)^2}{1 \cdot 2 \cdot 3 \cdot 4 \cdot \ldots \cdot 2N} \cdot \frac{1}{\sqrt{2N}} = \sqrt{\frac{\pi}{2}}$$

or, more briefly:

$$\text{Lim.} \frac{2^{2N} \cdot (N!)^2}{(2N)!} \cdot \frac{1}{\sqrt{N}} = \sqrt{\pi}$$

and hence, substituting from (382):

$$\text{Lim.}\, 2^{2N} \cdot \left(\frac{N}{e}\right)^{2N} f^2(N) \left(\frac{e}{2N}\right)^{2N} \frac{1}{f(2N)} \cdot \frac{1}{\sqrt{N}} = \sqrt{\pi}$$

This simplifies to:

$$\text{Lim.} \frac{f^2(N)}{f(2N)} \cdot \frac{1}{\sqrt{N}} = \sqrt{\pi}$$

This functional equation is satisfied by the assumption :

$$f(N) = \alpha \cdot N^{\beta} . \qquad (385)$$

For it gives :

$$\frac{\alpha^2 N^{2\beta}}{\alpha (2N)^{\beta}} \cdot \frac{1}{\sqrt{N}} = \sqrt{\pi}$$

from which :

$$\alpha = \sqrt{2\pi}, \quad \beta = \frac{1}{2}$$

Hence by (385) :

$$f(N) = \sqrt{2\pi N}$$

and by (382) :

$$N\,! = \left(\frac{N}{e}\right)^{N} \sqrt{2\pi N} \quad . \qquad (386)$$

This is Stirling's formula except that a factor has been neglected which becomes unity when N tends to infinity.

If we substitute the value (386) in the expression (381) for the statistical weight G of a macroscopic state given by the numbers N_0, N_1, N_2 . . ., we get :

$$G = \frac{\left(\frac{N}{e}\right)^{N}}{\left(\frac{N_0}{e}\right)^{N_0} \cdot \left(\frac{N_1}{e}\right)^{N_1} \cdot \left(\frac{N_2}{e}\right)^{N_2} \ . \ . \ .}$$

Factors have been neglected here which on account of their small order of magnitude make no appreciable difference. If we substitute for the index N from (379) we get :

$$G = \left(\frac{N}{N_0}\right)^{N_0} \cdot \left(\frac{N}{N_1}\right)^{N_1} \cdot \left(\frac{N}{N_2}\right)^{N_2} \cdot \ . \ . \ . \qquad (387)$$

or, written in a more convenient form :

$$\log G = - N \, . \sum_{n=0}^{n=\infty} w_n \log w_n \ . \qquad (388)$$

where :

$$w_n = \frac{N_n}{N} \quad . \quad . \qquad . \quad . \qquad (389)$$

denotes the so-called distribution number, which expresses the fraction of the elementary systems which has the energy ϵ_n in the macroscopic state assumed for the whole system. By (379) and (380) the distribution numbers fulfil the conditions :

$$\sum_0^\infty w_n = 1 \quad . \quad . \quad . \qquad (390)$$

and :

$$\sum_0^\infty w_n\epsilon_n = \frac{E}{N} = \bar{\epsilon} \qquad (391)$$

where $\bar{\epsilon}$ denotes the mean energy of an elementary system.

§ 124. The different macroscopic states which are possible for a definite value E of the energy of the total system will have very different statistical weights G and among them there will be one which has the greatest statistical weight. To determine it is a simple problem in the calculus of variations. Keeping N and E constant we vary all the distribution numbers by an infinitely small amount and seek out that distribution for which δG vanishes. From (388) we get for this :

$$\Sigma \log w_n \delta w_n + \Sigma \delta w_n = 0 \quad . \qquad (392)$$

in which, by (390) and (391) the conditions :

$$\Sigma \delta w_n = 0 \quad \text{and} \quad \Sigma \epsilon_n \delta w_n = 0$$

hold.

Eliminating by means of Lagrange's undetermined multipliers (I, § 97), we get :

$$\log w_n + \lambda + \mu\epsilon_n = 0$$

or :

$$w_n = \alpha \, . \, e^{-\beta\epsilon_n} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (393)$$

as the distribution which has the greatest statistical weight. The constants α and β are both positive ; the former because w_n is positive, the latter because w_n cannot become infinite when ϵ_n increases. Their values may be obtained from equations (390) and 391). From (390) :

$$\frac{1}{\alpha} = \Sigma e^{-\beta\epsilon_n}$$

and hence by (393):

$$w_n = \frac{e^{-\beta\epsilon_n}}{\Sigma e^{-\beta\epsilon_n}} \quad . \tag{394}$$

and then we get β from (391):

$$\frac{\Sigma\epsilon_n e^{-\beta\epsilon_n}}{\Sigma e^{-\beta\epsilon_n}} = \bar{\epsilon} = \frac{E}{N} \quad . \quad . \tag{395}$$

This is a transcendental equation in β. Hence it is often more convenient to regard, not E, but β as the independent parameter.

The value of the maximum of G is then obtained by substituting (393) in (388):

$$\left.\begin{aligned} \log G &= -N\Sigma w_n(\log\alpha - \beta\epsilon_n) \\ &= -N(\log\alpha - \beta\bar{\epsilon}) \\ &= N\log\Sigma e^{-\beta\epsilon_n} + \beta E \end{aligned}\right\} \tag{396}$$

Before we enter into the physical meaning of the energy distribution (393) that we have found we shall first briefly consider the type of maximum for log G represented by it. For this purpose we shall calculate the change in the value (388) of log G for any finite small variations Δ of the distribution numbers w_n. Thus:

$$\Delta\log G = -N\Sigma(w_n + \Delta w_n)\log(w_n + \Delta w_n) + N\Sigma w_n\log w_n$$

Now, since $\log(w_n + \Delta w_n) = \log w_n + \frac{\Delta w_n}{w_n} - \frac{1}{2}\left(\frac{\Delta w_n}{w_n}\right)^2$, in which we have neglected the smaller terms, it follows that the deviation of the statistical weight from its maximum value is:

$$\Delta\log G = -\frac{N}{2}\Sigma\frac{\Delta w_n{}^2}{w_n} \quad . \quad . \quad . \quad . \tag{397}$$

and this is in fact always negative. But we also see that even when the Δw_n's are small the deviation can become very great; this is always so when the Δw_n's exceed the order of magnitude $\frac{1}{\sqrt{N}}$. From this it follows *a fortiori* that for finite variations of the Δw_n's the change in log G assumes great values. In other words, the maximum of the statistical weight is very steep and very pronounced, and accordingly the energy distribution that corresponds to it is distinguished by being particularly sharp.

§ 125. Before proceeding to use the calculated statistical weight G of a given macroscopic state of our system in order to find its entropy and so to give it a thermodynamical meaning, we have first to fulfil an essential preliminary condition. We must do away with the assumption made in § 122 that the elementary configurations of which the system in question is composed are completely isolated from one another. For, as we see from the discussion in the preceding chapter, the statistical interpretation of the second law has a meaning only if the different microscopic states of a system can become interchanged in the course of time. But in the case where the elementary configurations are all isolated from one another each retains its energy unchanged for all time and a microscopic state that once exists continues without cessation. We are therefore compelled now to introduce an exchange of energy even if it be only small and quite irregular, or, to use the technical expression, we introduce a very loose coupling between the elementary systems. This loose coupling is to serve the sole purpose of allowing an elementary system here and there to change its state even if it occur only arbitrarily rarely. Then, on account of the interactions between the individual elementary systems, different microscopic states of the total configuration can relieve one another, and since all the microscopic states occur equally often, that microscopic state which occurs most often will be that to which the greatest number of microscopic states, that is, the greatest statistical weight, corresponds. Hence this state represents the state of thermodynamic equilibrium or of maximum entropy. On account of the steepness of the maximum (see end of § 124) the fluctuations of the entropy about the maximum value will always be very small and may be neglected if the N's are sufficiently great. By (372) and (396) the maximum value itself comes out as :

$$S = Nk \log \Sigma e^{-\beta\epsilon_n} + \beta k E \quad . \quad . \quad . \quad (398)$$

The temperature of the configuration is then also determined by the entropy.

To enable us to picture the state of affairs more easily we may imagine the coupling between the elementary configurations to be realized by placing them all in a common bath having the temperature of the whole system, and we shall suppose this bath to consist of a highly rarefied gas. We must of course bear in mind that by introducing a heat-bath as a means of communication between the elementary configurations the assumptions under which the results of the preceding section were deduced undergo a slight change. For the energy E of the whole system is no longer constant in time as now energy can be transferred to the heat-bath. Since, however, the relative fluctuations of energy in a gas containing a great number of moles are extremely small, as our calculation in § 120 shows, we may regard the equations (395) and (398), by which the entropy S is determined as a function of the energy in the state of thermodynamic equilibrium, as valid to an appreciable degree of accuracy.

It is important to remark that the substance and the constitution of the heat-bath used can exert no influence on the nature of the thermodynamic equilibrium. For if two different heat-baths have the same temperature then, by § 3, a body which is in thermal equilibrium with one of these heat baths will also be in equilibrium with the other. Hence we can speak of the entropy and hence also of the temperature of the configuration in question without referring to a heat-bath at all; this is actually expressed in equation (398).

The temperature T of the configuration and simultaneously the temperature of every heat-bath in equilibrium with the configuration are obtained from the entropy S by means of the general thermodynamic relation (106) between the entropy S and the energy E (called U in the equation) in the case of a configuration isolated from its surroundings :

$$\frac{1}{T}=\frac{dS}{dE} \quad . \tag{398a}$$

Since S cannot be expressed explicitly in terms of E, but only by way of the parameter β we write :

$$\frac{1}{T}=\frac{dS}{d\beta}\bigg/\frac{dE}{d\beta}$$

and determine the numerator of this quotient by (398) and the denominator by (395). Calculation gives :

$$\frac{1}{T}=k\beta \tag{399}$$

which closely relates the parameter β with the temperature T. So the equations (395) and (398) become :

$$E=N\bar{\epsilon}=N\cdot\frac{\Sigma\epsilon_n e^{-\frac{\epsilon_n}{kT}}}{\Sigma e^{-\frac{\epsilon_n}{kT}}} \tag{400}$$

and :

$$S=\frac{E}{T}+Nk\log\Sigma e^{-\frac{\epsilon_n}{kT}} \tag{401}$$

If we compare these equations with the general thermodynamic relations (112) and (126) we obtain the expressions for the characteristic function of the configuration :

$$\Psi=Nk\log\Sigma e^{-\frac{\epsilon_n}{kT}}=N\bar{\psi} \quad . \tag{402}$$

and for the free energy :

$$F=-NkT\log\Sigma e^{-\frac{\epsilon_n}{kT}} \quad . \quad . \quad . \tag{403}$$

As we see, all these functions and hence the whole thermodynamic behaviour of the configuration in question are essentially conditioned by the value of the sum :

$$\Sigma e^{-\frac{\epsilon_n}{kT}}=Z\,. \tag{404}$$

which is therefore called the "sum of the states" of an elementary system or configuration.

We also write down here, for later use, the general relations (114) and (128a):

$$E = T^2 \frac{d\Psi}{dT} \quad . \qquad (405)$$

and:

$$S = -\frac{dF}{dT} = \Psi + T\frac{d\Psi}{dT} \quad . \qquad (406)$$

which can easily be verified by means of the above expressions.

§ 126. We shall now consider more closely the physical properties of the statistical thermal equilibrium that has been found. The distribution number corresponding to a definite amount of energy ϵ_n of an elementary configuration is, by (394) and (399):

$$w_n = \frac{e^{-\frac{\epsilon_n}{kT}}}{\Sigma e^{-\frac{\epsilon_n}{kT}}} \quad . \qquad (407)$$

It represents the mathematical probability that any arbitrarily chosen elementary configuration should have the energy ϵ_n. Hence the smallest energy ϵ_0 is most frequently represented; this is followed by the increasingly greater amounts of energy ϵ_1, ϵ_2 . . ., which occur less and less frequently.

But we may also give the distribution numbers w another meaning. For since the elementary systems are all of the same kind, they also pass through the same changes of state in time, and these changes of state taken together condition the various microscopic states of the total configuration. According to this view w_n in (407) simultaneously denotes the probability that, when we consider the changes which a definite individual elementary system undergoes in the course of time, the energy ϵ_n should occur at an arbitrarily chosen point of time. In considering the time changes of state of an individual elementary system we must of course regard them as caused by the action of the heat-bath since this is the only body that affects the elementary system. Otherwise the temperature would not be defined at all.

So we see *that the energy of an individual elementary system which is in a heat-bath of temperature T but otherwise completely heat-insulated performs quite definite fluctuations as represented by* (407); these fluctuations depend only on the temperature and not on the nature of the heat-bath. Since the mean energy $\bar{\epsilon}$ will in general differ considerably from the most frequently occurring energy ϵ_0, the difference of the momentary energy ϵ_n from the mean energy $\bar{\epsilon}$ will as a rule be very appreciable, being sometimes negative and sometimes positive. To obtain a quantitative measure of these deviations from the mean value, which are also denoted by the terms "scattering" or "dispersion," we cannot of course simply form the mean value of the difference $\epsilon_n - \bar{\epsilon}$; for its value is zero. But we arrive at a serviceable measure of the scattering if we form the mean value of the square of the difference $(\epsilon_n - \bar{\epsilon})^2$; this is called the "mean square fluctuation." If this quantity is very small any appreciable deviations from the mean value will occur only rarely. To make the value of the mean square fluctuation independent of the units chosen we form the "relative" mean square fluctuation:

$$\Delta = \frac{\overline{(\epsilon_n - \bar{\epsilon})^2}}{\bar{\epsilon}^2} \tag{408}$$

The numerator of this expression is:

$$\overline{(\epsilon_n - \bar{\epsilon})^2} = \overline{\epsilon^2} - 2\bar{\epsilon}\bar{\epsilon} + \bar{\epsilon}^2 = \overline{\epsilon^2} - \bar{\epsilon}^2$$

Hence:

$$\Delta = \frac{\overline{\epsilon^2}}{\bar{\epsilon}^2} - 1 \quad . \tag{409}$$

Whereas the mean energy $\bar{\epsilon}$ is obtained by (400) directly from the total energy E the mean square energy:

$$\overline{\epsilon^2} = \Sigma \epsilon_n^2 w_n = \frac{\Sigma \epsilon_n^2 e^{-\frac{\epsilon_n}{kT}}}{\Sigma e^{-\frac{\epsilon_n}{kT}}} \tag{410}$$

may be derived from (400) by differentiating with respect to the temperature. For if we perform this differentiation and simplify we get :

$$\frac{dE}{dT} = \frac{N}{kT^2}(\overline{\epsilon^2} - \bar{\epsilon}^2)$$

and so, taking into account (409) :

$$\Delta = \frac{kT^2}{\bar{\epsilon}^2} \cdot \frac{d\bar{\epsilon}}{dT} = - kT^2 \frac{d}{dT}\left(\frac{1}{\bar{\epsilon}}\right) \quad . \quad . \quad (411)$$

This enables us to state the value of the relative mean square fluctuation as soon as we have calculated by (400) how the mean energy $\bar{\epsilon}$ depends on the temperature T. To do this we must of course know the energy values ϵ_n of the elementary system, concerning which we have made no assumptions at all so far. But we may take this opportunity of giving as a striking example of the energy fluctuations of an individual elementary system in a heat-bath the motion of a fine particle of dust suspended in a liquid; this is the so-called "Brownian movement" which is the more vigorous the smaller the particle, because for a definite energy-fluctuation of a moving point-mass the fluctuation of velocity increases as the mass decreases.

§ 127. Hitherto we have assumed in our elementary system that there is a perfectly definite microscopic state of the system corresponding to every possible quantity of energy ϵ_n of it. This will be so only in the case of systems of quite simple construction. In general, however, and particularly when the elementary system has a rather large number of degrees of freedom, we shall also have to take into consideration the case where every possible amount of energy ϵ_n has several or even many different microscopic states of the configuration belonging to it. In such a case we call the configuration "degenerate." The question now is how can the laws which have so far been found to be valid for a group of elementary systems of exactly the same kind be generalized for the cases where the elementary systems are degenerate to a greater or a lesser degree. This question can be answered by the simple procedure of passing to the limit. For since we have made no assumptions about the quantities ϵ_n of energy nothing prevents us from assuming the elementary system—at present non-degenerate—to be such that the possible energies accumulate in groups in the immediate neighbourhood of certain favoured values; we may, then, without introducing an appreciable error, comprise all terms that belong to such a group in a single term:

$$g_n e^{-\frac{\epsilon_n}{kT}}$$

in the sum of the states as expressed by (404). Here ϵ_n denotes the energy at the point of accumulation, g_n the number of microscopic states that constitute the group. The sum of the states then runs:

$$Z = \Sigma g_n e^{-\frac{\epsilon_n}{kT}} \quad . \quad . \quad . \qquad (412)$$

and, by (402), the characteristic function is:

$$\Psi = Nk \log Z = N\bar{\psi} . \quad . \quad . \quad . \qquad (413)$$

Hence by (405) the energy is:

$$E = N \cdot \frac{\Sigma g_n \epsilon_n e^{-\frac{\epsilon_n}{kT}}}{\Sigma g_n e^{-\frac{\epsilon_n}{kT}}} = N \cdot \bar{\epsilon} \quad . \quad . \qquad (414)$$

Now if the energies of a group draw together more and more closely the configuration finally merges into a degenerate system with g_n microscopic states corresponding to every possible amount of energy ϵ_n. This number g_n is called the statistical weight of the energy ϵ_n or the degree of degeneracy. The introduction of the statistical weight g_n in the expression for the sum of the states thus makes all the previous laws valid also for a family of degenerate systems.

A very important consequence follows on this generalization. For let us again consider an individual elementary configuration in a heat-bath of temperature T and let us investigate the fluctuations which its energy undergoes. According to (407) these may be represented by the distribution number :

$$w_n = \frac{g_n e^{-\frac{\epsilon_n}{kT}}}{\Sigma g_n e^{-\frac{\epsilon_n}{kT}}} \tag{415}$$

So long as g_n was equal to 1 we had to conclude that the smallest amount of energy ϵ_0 occurred most frequently. The position is, however, now altered. For if the elementary configuration is degenerate, as, for example, when it contains many degrees of freedom by consisting, say, of many oscillators, the statistical weight g_n with the ordinal number n will rapidly increase, since a greater amount of energy ϵ_n will be able to distribute itself over the different degrees of freedom in many more different ways than a smaller amount of energy. Thus as n increases the numerator of (415) will also at first increase; but later, when the ϵ_n's become sufficiently great, it will sink to vanishingly small values on account of the exponential function. The maximum of w_n, the point when the most frequent energy occurs, thus no longer lies at $\bar{\epsilon}_0$ but is displaced towards $\bar{\epsilon}$; that is, the energy fluctuations are less than in the case of a non-degenerate configuration.

A quantitative measure of the scattering is given by the relative mean square fluctuation Δ, whose amount, also for a non-degenerate elementary system, is again represented by the expression (411), as is easily seen by differentiating the equation (414) with respect to T. The greater the degree of degeneracy, the more the number of degrees of freedom possessed by the elementary system, and the greater the mean energy $\bar{\epsilon}$ of the system corresponding to a definite temperature T of the heat-bath will be, for the simple reason that the total energy of many oscillators becomes infinite when their number becomes infinitely large. From this it follows by (411) that the value of Δ becomes vanishingly small for a highly degenerate elementary system, or that the distribution number w_n in (415), regarded as a function of ϵ_n, possesses a narrow and steep maximum.

In other words, *an elementary system of many degrees of freedom in a heat-bath of definite temperature T performs only very small relative energy fluctuations*, and the energy that occurs most frequently coincides appreciably with the mean energy $\bar{\epsilon}$. Hence an elementary system having many degrees of freedom will have at every temperature a perfectly definite energy $\bar{\epsilon}$ given by (414); and, of course, conversely for every amount of energy there is a perfectly definite temperature, so that we can speak of the temperature of the elementary system in a definite sense without referring to the temperature of the heat-bath.

Now since we have made no hypothesis about the constitution of an elementary system, there is nothing to prevent our treating *any body whatsoever*—so long as it is not too small—which has quite arbitrary macroscopic properties, as an individual elementary system, and so applying to it the equations (412) and (413). Now if we indicate the occurrence of many degrees of freedom by writing E for $\bar{\epsilon}$, G for g and Ψ for $\bar{\psi}$, omitting the bars, which have now become superfluous, the equations just mentioned become:

$$Z = \Sigma G_n e^{-\frac{E_n}{kT}} \quad . \quad . \quad . \quad . \quad . \qquad (416)$$

$$\Psi = k \log Z = k \log \Sigma G_n e^{-\frac{E_n}{kT}} . \quad . \qquad (417)$$

This equation determines how the function Ψ depends on the temperature T and so fixes the whole thermodynamic behaviour of the system. It is completely equivalent to the relation (372) by which the entropy S is determined when the energy E is given. For by § 55 Ψ is the characteristic function when the temperature T is the independent variable, whereas when the energy E is the independent variable the entropy S, by § 54, represents the characteristic function.

Just as by starting from (372) we arrive at (417) so, conversely, we can derive the relation (372) from (417), the way being very direct. For if we reflect that in the sum of the states (416), on account of the narrow and steep maximum of the distribution numbers, all those terms are inappreciable whose energy E_n deviates markedly from the most frequent or mean value, we may write the mean value of the energy E instead of E_n in all the terms that come into question. The sum of the states then assumes the form :

$$Z = G \, . \, e^{-\frac{E}{kT}}$$

where G now denotes the sum of the statistical weights of all those states of the system in which the energy differs only slightly from E and in so far as they contribute appreciably to the sum of the states. Hence the characteristic function by (417) becomes :

$$\Psi = k \log G - \frac{E}{T}.$$

If we compare this relation with the general thermodynamic relation (112) in which the energy is denoted by U, we get :

$$S = k \log G \quad . \quad . \quad . \quad . \qquad (418)$$

which has brought us back to the relation (372).

But there still remains an unsatisfactory discrepancy which requires to be elucidated. It consists in the fact that in (372) the quantity G refers to a perfectly definite amount of energy E whereas in (418), as we expressly remarked, G also includes those states whose energy deviates slightly from E. This difficulty resolves itself when we consider that in forming the quantity G in (372) the energy E of the system is to be regarded as determinate only in a macroscopic sense and that a value which has been determined in this way still allows small deviations, in complete analogy with the small fluctuations of energy considered in § 120. How far the deviations of the energy from the macroscopically given value E may and must be taken to include exactly all the states that contribute appreciably to the value of the statistical weight G is determined by the circumstance that an increase of the deviation must produce no appreciable change in the value of G.

But an essential point must be noted here. In the expression (417) of the characteristic function Ψ the summation formula is to be taken over all the energies E_n of the system, from 0 to ∞. As we have seen, the sum of the states then involves only those terms whose energy E_n differs but little from the mean value E. The steepness of the maximum at the point $E_n = E$ is caused on the one side, $E_n < E$, by the first factor, G: on the other side, $E_n > E$, it is due to the second factor, the exponential function. On the other hand, in the expression (372) for the entropy S the second factor is absent. Consequently, in forming S by means of (372), we may not count microscopic states whose energy exceeds the macroscopically given energy E in the upward direction, whereas in the downward direction the deviation may be as great as we please.

In other words, *the statistical weight G which must be substituted in* (372) *to give the value of the entropy S of a physical system of given energy E is appreciably equal to the total number of microscopic states of the system whose energy does not exceed the value E.*

At first sight it may seem strange that although *all* the microscopic states with arbitrarily small amounts of energy are used to form the total number G the value of G yet essentially depends only on such states as have energies that lie near the maximum energy; that is, that the number of all those microscopic states whose energy is appreciably less than E is of no account compared with the number of those whose energy lies near the value E. We are tempted to surmise that a small increase in the energy $\Delta E \ll E$ would of necessity correspond to only a small increase $\Delta G \ll G$ of the number of all the microscopic states that are possible between 0 and E. A simple example shows that this is not so. Let $G = E^f$. Then for a given $\Delta E \ll E$, no matter how small ΔE is, we can always choose the number f to be so great that $\Delta G = (E + \Delta E)^f - E^f \gg G$.

The circumstances are exactly similar in our present case. All we require to do is to assume the number of degrees of freedom of the physical system under consideration to be so great that contributions to the value of the statistical weight calculated according to the above rule are made only by those microscopic states whose energies lie near the value of the energy of the system. If this condition is incapable of fulfilment there is no definite entropy at all corresponding to a definite energy E of the system. And then we can speak of the temperature of the system, too, only in the sense that if we place it in a heat-bath of a definite temperature the energy of the system undergoes the familiar more or less appreciable fluctuations.

Numerical examples proving the validity of all these laws may be obtained from the special applications given in the next chapter.

§ 128. To evaluate the sum of the states Z it is often more convenient to replace the expression (416) by another in which we write down individually the microscopic states that have a common energy E_n, thus:

$$Z = \sum_n G_n e^{-\frac{E_n}{kT}} = \sum_z e^{-\frac{E_n}{kT}} \tag{419}$$

and:

$$\Psi = k \log \sum_z e^{-\frac{E_n}{kT}} \tag{420}$$

The index z is to denote that the summation is to be performed not over the order numbers n of the energy but over the individual states, so that every amount of energy E_n is counted just as many times as there are states which have this amount of energy. Thus the sum in (420) simply includes all the microscopic states of the system, from the smallest amount of energy to the greatest, and to perform the summation we may arrange the terms of the sum in any order.

The equation (420) is considerably more general than the equation (402), although it looks quite similar. For it is valid for any system whatsoever of many degrees of freedom, while (402) holds only for those which are composed of N components which are independent of one another *but are of the same kind.* Since the latter is a special case it is evident that the equation (402) can be derived from (420). We show this in the following way. If the system consists of a great number N of elementary systems which are of the same kind but independent of one another and non-degenerate, their energies being assumed to be $\epsilon_0, \epsilon_1, \epsilon_2, \ldots \epsilon_n, \ldots$, then any possible value of the whole system is given by :

$$\epsilon_n + \epsilon'_{n'} + \epsilon''_{n''} + \ldots = E$$

where the individual sums refer to the individual elementary systems, and so by (420) :

$$\Psi = k \log \sum_n \sum_{n'} \sum_{n''} \ldots e^{-\frac{\epsilon_n + \epsilon'_{n'} + \epsilon''_{n''} + \ldots}{kT}}$$

Since there is a microscopic state corresponding to every combination of the order numbers $n, n', n'' \ldots$, and conversely, the summation must be performed over every order number from 0 to ∞. The exponential function resolves into a product of corresponding exponential functions having one order number each. If we now sum over the order number n, keeping all the other order numbers fixed, we get the following sum, a constant factor being disregarded :

$$\sum_n e^{-\frac{\epsilon_n}{kT}}$$

And by continuing this process we get, since this sum is the same for all the N kinds of order numbers :

$$\Psi = k \log \left(\sum_n e^{-\frac{\epsilon_n}{kT}} \right)^N$$

which is identical with the equation (402).

CHAPTER III

CLASSICAL THEORY. LIOUVILLE'S THEOREM. QUANTUM STATISTICS

§ 129. THE laws which have been derived in the two preceding chapters represent the methods which enable us to determine the characteristic function and hence the whole thermodynamic behaviour of a given physical system. They prescribe the line of reasoning which must be followed in *every* statistical theory of heat. But to be able to fill the form that has been obtained with content we have yet to know the values E_n, which the energies of the system can assume, as well as the corresponding statistical weights G_n. This is the point where the different statistical theories diverge, namely the theories of Boltzmann and Gibbs, of Bose and Einstein, and of Pauli, and Fermi and Dirac.

As an introduction to this complex of problems we find it advantageous to start out from *classical statistics* not only because it is the oldest but rather because it links up most directly with classical mechanics and electrodynamics, and also because it is necessary on the one hand to convince oneself of its insufficiency and, on the other hand, to establish the limits within which it is valid. Let us consider any mechanical system completely isolated from its surroundings and having f degrees of freedom, where f is an arbitrarily great or small integer, then by the classical theory the state of the system is determined by $2f$ quantities, namely by the f general co-ordinates q_1, q_2, . . . q_f and the f corresponding velocities $\dot{q}_1$, $\dot{q}_2$, . . . $\dot{q}_f$ (I, § 124). The sum total of all the possible states of the system thus forms a continuously extended manifold of $2f$-dimensions (§ 117), which is most easily pictured by considering a space of $2f$-dimensions, called "phase-space," whose rectangular co-ordinates are the quantities q and $\dot{q}$. Then for every point of the phase-space there is a definite state of the system. Further, by the laws of classical mechanics, the state at any particular moment of time determines the whole motion, that is, the succession of states for all subsequent times. This expresses itself in phase-space in the fact that every phase-point traverses a perfectly definite curve with a definite velocity. This curve is called the "phase-orbit." Since the phase-points fill the phase-space continuously all these motions together present the picture of a flowing liquid, and the stream is stationary because the velocity and the direction of flow at every point of the phase-space are independent of the time. Thus if we consider any arbitrary region of the phase-space all the points of this region will move in a definite way and so we may say that every region of the phase-space displaces itself in a definite way in the course of time and becomes deformed.

§ 130. The problem with which we are now confronted is as follows. What number of microscopic states of the system is contained in a given region of phase-space? For by our definition (§ 117) this number represents the statistical weight or the thermodynamic probability of the whole region.

In the first place it is clear that in this form of the question the answer of the classical theory can only be "infinitely great." For by classical theory the microscopic states and the phase-points corresponding to them form a continuous manifold. Hence it follows that the classical theory can give only a relative and not an absolute answer to the question by fixing a more or less arbitrary measure for the unit of statistical weight. Now since the greater the number of microscopic states contained in a given phase-region the more extended it is, we find it appropriate to set the statistical weight of a given phase-region proportional to the extent or the "volume" of this region, that is, to the quantity :

$$\int d\tau,$$

where $d\tau = dq_1 . dq_2 \ . \ . \ . \ dq_f . d\dot{q}_1 . d\dot{q}_2 \ . \ . \ . \ d\dot{q}_f$. Accordingly, the statistical weight of this region is :

$$G = C . \int d\tau \ . \qquad (421)$$

where the factor of proportionality C denotes a certain infinitely great universal constant, which remains indeterminate and arbitrary.

Nevertheless this definition still suffers from a serious fault. For if we apply it to calculate the statistical weight of a definite region in phase-space the result comes out very differently according to the choice of the co-ordinates q, and—a no less serious matter—it changes its value in the course of time corresponding to the deformation of the region which was mentioned at the end of the preceding section ; this is incompatible with a general theorem of the theory of probability, which demands that a state which necessarily emerges from another state must also have the same probability as the latter state.

A theorem proposed by Liouville offers an escape from this difficulty. For if we use as the co-ordinates of the phase-space besides the f generalized co-ordinates q of the system the corresponding f momentum-co-ordinates p (I, § 128) in place of the velocities $\dot{q}$, and if we define as the element of volume of the phase-space the differential :

$$d\tau = dq_1 . dq_2 \ . \ . \ . \ dq_f . dp_1 . dp_2 \ . \ . \ . \ dp_f \ . \quad . \qquad (422)$$

then *the quantity* G *in* (421) *is, for a given region of the phase-space, independent of both the choice of co-ordinates* q *and the time.*

We first prove the latter assertion. We proceed by considering an extremely small region of phase-space at the time t in the form of a $2f$-dimensional rectangular parallelepiped whose edges are parallel to the co-ordinate axes of the phase-space. The volume of this region is :

$$\Delta\tau = \Delta q_1 . \Delta q_2 \; . \; . \; . \; \Delta p_1 . \Delta p_2 \; . \; . \; .$$

After the lapse of an infinitely small interval of time, during which the co-ordinates of every phase-point have changed by :

$$dq_1 = \dot{q}_1 dt,\; dq_2 = \dot{q}_2 dt \; . \; . \; . \; dp_1 = \dot{p}_1 dt,\; dp_2 = \dot{p}_2 dt \; . \; . \; .$$

all the phase-points belonging to the selected region again form approximately a rectangular parallelepiped of size :

$$\Delta\tau' = \Delta(q_1 + \dot{q}_1 dt) . \Delta(q_2 + \dot{q}_2 dt) \; . \; . \; . \; \Delta(p_1 + \dot{p}_1 dt) . \Delta(p_2 + \dot{p}_2 dt) \; . \; . \; .$$

where we neglect terms of vanishingly small order of magnitude.

If we now reflect that in the preceding expression :

$$\Delta\dot{q}_1 = \frac{\partial \dot{q}_1}{\partial q_1} . \Delta q_1, \; . \; . \; . \; \Delta\dot{p}_1 = \frac{\partial \dot{p}_1}{\partial p_1} . \Delta p_1, \; . \; . \; .$$

in which all the remaining co-ordinates are kept constant during the differentiations, we get for the change of size of the phase-region, disregarding vanishingly small quantities :

$$\Delta\tau' - \Delta\tau = \Delta\tau . \left(\frac{\partial \dot{q}_1}{\partial q_1} + \frac{\partial \dot{q}_2}{\partial q_2} + \; . \; . \; . + \frac{\partial \dot{p}_1}{\partial p_1} + \frac{\partial \dot{p}_2}{\partial p_2} + \; . \; . \; .\right) . dt$$

and, by the equations of motion (413) of § 128, Vol. I, this expression is equal to zero.

Thus an arbitrarily selected part of phase-space :

$$\Delta\tau = \int\!\!\int dq_1 \; . \; . \; . \; dp_1 \; . \; . \; . \; . \qquad (423)$$

does not change in size if all points of the region move in their phase-orbits in accordance with the equations of dynamics. Hence our above model of a stationary flow of liquid becomes further specialized by the condition that the liquid must be incompressible.

§ 131. Let us here interpolate an interesting consequence of the last result which immediately suggests itself. If, starting from any arbitrary point of a phase-orbit, we follow this orbit for a sufficiently long time we shall ultimately arrive at the starting-point exactly or at least to any desired degree of approximation, so long as we assume that phase-space extends to infinity in no direction whatsoever (Poincaré's Recursion Law, *Wiederkehrsatz*). For since the flowing liquid is incompressible the space traversed by the cross-section of a thin current-filament (II, § 61) will in the course of time exceed any arbitrary quantity no matter how thin the filament may be chosen. And if the volume of the whole of phase-space is finite this can happen only if the current-filament either returns exactly into itself—the motion is then periodic—or at least meets itself again at some point.

§ 132. We have yet to prove that the value of the integral (423) taken over a definite region of phase-space is independent of the choice of co-ordinates q. This may be shown as follows. If in place of the co-ordinates q_1, q_2, . . . q_f we introduce any other co-ordinates ϕ_1, ϕ_2, . . . ϕ_f where the co-ordinates ϕ are functions of the co-ordinates q then our object is to compare the quantity (423), which we shall denote by $\Delta\tau_q$ for the sake of clearness, with the quantity :

$$\Delta\tau_\phi = \int\int d\phi_1 \ . \ . \ . \ d\psi_1 \ . \ . \ . \qquad (424)$$

where the ψ's are the momentum co-ordinates corresponding to the co-ordinates ϕ, and the contour of the integral (424) corresponds with that of (423). We choose the region $\Delta\tau_q$ to be very small and hence also the region $\Delta\tau_\phi$.

If we now allow a comparatively long time to pass, say from t to t', the region $\Delta\tau_q$ will have moved a considerable distance from its original position and will be in a distant part of phase-space. The region $\Delta\tau_\phi$ will likewise have moved a long way from its original position. By Liouville's Theorem we have that :

$$\Delta\tau'_q = \Delta\tau_q \quad \text{and} \quad \Delta\tau'_\phi = \Delta\tau_\phi .$$

We shall next introduce a third kind of co-ordinates $x_1, x_2, \ldots x_f$, which are also definite functions of the co-ordinates q. But we shall choose these co-ordinates in such a way that in the original portion of phase-space they coincide with the co-ordinates q except for inappreciable deviations, whereas in the distant region of the phase-space they coincide with the co-ordinates ϕ. There is nothing to prevent this choice since no restriction has been imposed on the functional relationship between the co-ordinates. Since the momentum co-ordinates are completely determined by the generalized space co-ordinates—for we are dealing with a perfectly definite motion—the same is true of the momentum co-ordinates ξ that belong to x. We therefore have :

$$\Delta\tau_q = \Delta\tau_x \quad \text{and} \quad \Delta\tau'_\phi = \Delta\tau'_x$$

But according to Liouville's Theorem :

$$\Delta\tau_x = \Delta\tau'_x$$

and consequently, by the preceding relations :

$$\Delta\tau_\phi = \Delta\tau_q,$$

which was to be proved.

§ 133. After having justified, so far as is possible from the point of view of classical theory, the definition of the statistical weight G of a definite region in phase-space by means of the equation (421) in conjunction with the expression (422) for $d\tau$ we may use it directly in (418) to calculate the entropy S for the case of a configuration having many degrees of freedom. On account of taking logs, an additive infinitely great universal constant log C occurs which is indeterminate and hence remains arbitrary. In classical theory the entropy therefore has no definite value. But this does not make it impossible to draw certain definite conclusions from the entropy in the classical theory, since in differentiating the entropy the indeterminate additive constant disappears. So its presence is not in itself a reason for giving up the classical theory. In the hands of L. Boltzmann it has, indeed, led to far-reaching consequences which agree excellently with experimental results. Nevertheless, among the results of the classical theory we shall also become acquainted with some that are violently opposed to the results of experiment (§ 139). It is this which has led to the introduction of the *quantum theory.*

According to the quantum theory the statistical weight G of a definite region of phase-space or the number of microscopic states contained in this region is a definite finite number. This hypothesis leads to a totally new view of the concept of a microscopic state. For in classical theory a definite *point* in the phase-space is assigned to each microscopic state.

But if, as in the quantum theory, an arbitrarily great region of $2f$-dimensional space is to contain a finite number of microscopic states it is evident that to every individual microscopic state there is assigned a $2f$-dimensional *region* of phase-space. The size of this region, which we may call an " elementary region " or " element " of the phase-space, is obtained if we set $G = 1$ in (421), that is :

$$\int d\tau = \frac{1}{C} \tag{425}$$

which is a relatively small but finite universal constant. In general the statistical weight of a phase-region is then equal to the number of elements included in the phase-region.

We see that by these theorems the classical concept of the "state" of a mechanical system becomes fundamentally changed, or, we may say, blurred. In the quantum theory the state comprises, not a single phase-point, but all the points of a whole phase-orbit, and the phase-orbits, each of which indicates a definite energy, form a discrete manifold in the phase-space which can be counted. An individual element of phase-space is $2f$-dimensional; it thus forms a " current-filament " of finite though small cross-section, and the phase-orbits allowed by the quantum theory form the boundary of the current-filament.

However strange these deductions may sound, they have nevertheless in many cases stood the test of experiment and hence have led to radical changes in the theory: the complete explanation has only recently been given by wave-mechanics.

The following simple consideration is sufficient for our purpose. The universal constant $\frac{1}{C}$ in (425) has the dimensions $d\tau$ and hence, by (422), the dimensions of the fth power of the product $q.p$. By I, § 128, this product $q.p$ has the dimensions of energy multiplied by time, that is, of "action." Hence we set:

$$\frac{1}{C} = h^f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (426)$$

and we call the universal constant h the "elementary quantum of action." From this we get the following value for the size of an element of volume of phase-space:

$$\int d\tau = h^f . \quad . \quad . \qquad (427)$$

where $d\tau$ stands for the expression given in (422). And the statistical weight of an arbitrarily great volume of phase-space comes out, by (421), as:

$$G = \frac{1}{h^f} \cdot \int d\tau \quad . \quad . \quad . \quad . \quad . \quad . \qquad (428)$$

But it must be observed that this relation has a meaning only if the phase-volume contains an integral number of elements of volume. Since, however, the definition (418) for the entropy holds only for systems having very many degrees of freedom no essential limitation is imposed by the condition just stated.

§ 134. Although by introducing the elementary quantum of action into thermodynamic statistics we have diverged appreciably from classical theory, there is nothing to prevent our reverting to it at any moment. We have only to make h infinitely small to regain from (426) the constant C of the classical theory with all its properties. This circumstance will be of frequent use to us in the sequel. For it enables us by means of a simple mathematical operation to write alongside every quantum formula the corresponding classical formula and so to compare directly any laws given by the classical theory with those of the quantum theory.

CHAPTER IV

SIMPLY PERIODIC OSCILLATORS. ENERGY DISTRIBUTION IN THE NORMAL SPECTRUM

§ 135. In applying the theory developed above to special cases we have always the choice of two different methods. We either calculate the entropy S as a function of the energy E by the formula (418), or we calculate the characteristic function Ψ as a function of the temperature T by the formula (420). Since both methods lead to the same result our choice must be guided by practical considerations. We shall use the second method in the sequel, for two reasons. Firstly because the summation (420) can be effected more conveniently than the calculation of G in (418), since the former applies to *all* the states of the system whereas in the latter the boundary condition which corresponds to the given value of E must be taken into consideration. Secondly the temperature T is found to be more appropriate as the independent variable for the experimentally important consequences than the energy E.

We begin our calculations by considering a system which consists of a great number N of similar simply periodic oscillators isolated from each other, each having one degree of freedom in the sense of § 122. The law of motion of a simply periodic oscillator is expressed by the following differential equation (I, § 12) in the generalized co-ordinate of position q:

$$\ddot{q} + 4\pi^2\nu^2 q = 0 \quad . \quad . \quad . \quad . \quad (429)$$

where ν is the vibration number, or by its integral:

$$q = a \cos 2\pi\nu t + \beta \sin 2\pi\nu t \quad . \quad . \quad . \quad (430)$$

where a and β denote the two integration constants.

The energy is :

$$\epsilon = \frac{m}{2}\dot{q}^2 + 2\pi^2 m\nu^2 q^2$$

$$= 2\pi^2 m\nu^2(\alpha^2 + \beta^2) \quad . \quad . \quad . \quad (431)$$

where m denotes the mass, and the momentum co-ordinate has the value :

$$p = \left(\frac{\partial\epsilon}{\partial\dot{q}}\right)_q = m\dot{q} \qquad (432)$$

We have first of all to determine the discrete series of the quantities ϵ_0, ϵ_1, ϵ_2 . . ., the so-called proper-values of the energy. The equation (427) serves for this purpose. Since $f = 1$ here the phase-space is a plane, and the phase-orbits or the "stream lines" or "lines of flow" (§ 129) are the curves :

$$\epsilon = \frac{p^2}{2m} + 2\pi^2 m\nu^2 q^2 = \text{const.}$$

in the co-ordinates q and p.

These are similar and similarly situated ellipses having the semi-axes :

$$a = \sqrt{2m\epsilon} \quad \text{and} \quad b = \sqrt{\frac{\epsilon}{2\pi^2 m\nu^2}} \quad . \quad . \quad (433)$$

Corresponding to every ellipse there is a definite amount of energy. In classical theory every point of the phase-plane represents a possible microscopic state of the oscillator, but in the quantum theory we have, corresponding to a microscopic state, a whole "current-filament" of finite cross-section, namely the intermediate space between two different ellipses; the area of this space is, by (427), of amount h. Only the two boundaries of the current-filament, say the ellipses with the energies ϵ_n and ϵ_{n-1} have a physical meaning. Now since the area of an ellipse is, by (433) :

$$\pi ab = \frac{\epsilon}{\nu}$$

it follows from (427) that the intermediate space is :

$$\frac{\epsilon_n - \epsilon_{n-1}}{\nu} = h.$$

Likewise :

$$\frac{\epsilon_{n-1} - \epsilon_{n-2}}{\nu} = h$$

and so forth, down to :

$$\frac{\epsilon_1 - \epsilon_0}{\nu} = h.$$

By adding these equations we get :

$$\epsilon_n = \epsilon_0 + nh\nu \quad . \quad . \quad . \quad . \qquad (434)$$

This relation contains the law which governs the quantising of a simply periodic oscillator. We shall leave the value of the smallest amount of energy $\epsilon_0 < h\nu$ undetermined for the present.

Since corresponding to every amount of energy ϵ_n of the oscillator there is a single microscopic state, the elementary system is non-degenerate and so the relations deduced in Chapter II hold for this case of a system composed of a great number N of such oscillators of one and the same type. In particular the sum of the states at the temperature T is, by (404) and (434) :

$$Z = e^{-\frac{\epsilon_0}{kT}} \cdot \sum_{n=0}^{n=\infty} e^{-\frac{nh\nu}{kT}} = \frac{e^{-\frac{\epsilon_0}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} \quad . \quad . \qquad (435)$$

and, by (402), the characteristic function of the whole system is :

$$\Psi = -\frac{N\epsilon_0}{T} - Nk \log\left(1 - e^{-\frac{h\nu}{kT}}\right) . \qquad (436)$$

From this we get for the energy by (405) :

$$E = N \, . \, \bar{\epsilon} = N\epsilon_0 + \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1} \quad . \qquad (437)$$

and for the entropy, by (406):

$$S = \frac{1}{T} \cdot \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1} - Nk \log\left(1 - e^{-\frac{h\nu}{kT}}\right) . \qquad (438)$$

If the temperature increases to an unlimited extent the exponential function $e^{\frac{h\nu}{kT}}$ merges into $1 + \frac{h\nu}{kT}$, and the expressions for the energy and the entropy become:

$$E = NkT,\ S = Nk \log \frac{ekT}{h\nu} . \qquad (439)$$

The same expressions are obtained if for any arbitrary temperature T the quantum of action h is assumed to be infinitely small, but we must observe that when h becomes vanishingly small $\epsilon_0 < h\nu$ also vanishes. Hence by § 134 the expressions (439) also represent the values of the energy and the entropy that follow from the classical theory for the system in question. In particular, we see that according to the classical theory the mean energy is $\bar{\epsilon} = kT$ and so is independent of the nature (period of vibration) of the oscillators. It is in this deduction that the classical law of *equipartition of energy* over all the different kinds of oscillators expresses itself.

On the other hand, with unlimited decreasing temperature the energy of the system becomes by (437):

$$E = N . \bar{\epsilon} = N\epsilon_0 + Nh\nu e^{-\frac{h\nu}{kT}} . \qquad . \quad (440)$$

and the entropy, by (438):

$$S = \frac{Nh\nu}{T} \cdot e^{-\frac{h\nu}{kT}} \qquad (441)$$

Hence, whereas the entropy converges to zero together with the temperature, a finite amount of energy remains left over at zero temperature. This is the "zero point energy," which is easy to understand since the energy of an oscillator cannot fall below ϵ_0.

A single oscillator which is immersed in a heat-bath at a temperature T undergoes fluctuations of energy, which are regulated according to (407) and (434) by the law:

$$w_n = e^{-\frac{nh\nu}{kT}} \cdot \left(1 - e^{-\frac{h\nu}{kT}}\right) \quad . \qquad (442)$$

This expresses the mathematical probability that the oscillator will have the energy $\epsilon_n = \epsilon_0 + nh\nu$ at any moment. The relative mean square of the fluctuation will be given by (411). It assumes a particularly simple value if we set the zero-point energy $\epsilon_0 = 0$. Then we get, by (437):

$$\frac{d}{dT}\left(\frac{1}{\bar{\epsilon}}\right) = -\frac{1}{kT^2} e^{\frac{h\nu}{kT}}$$

and by (411):

$$\Delta = e^{\frac{h\nu}{kT}} = 1 + \frac{h\nu}{\bar{\epsilon}} \quad . \qquad . \qquad (443)$$

The relative mean square of the fluctuation of the energy thus consists of two parts: a constant term of the amount 1 and a term proportional to the quantum of action h and the vibration number ν and inversely proportional to the mean energy $\bar{\epsilon}$. In the classical theory the second term vanishes and fluctuations of only the first kind remain.

§ 136. Let us glance at the case when the number of oscillators N is not very great but has arbitrary values down to 1. In this case there is not a definite energy E of the system corresponding to a definite temperature T, but the system performs energy fluctuations, whose scattering, by § 127, is again represented by the relative mean square of the fluctuations (411) if we substitute for $\bar{\epsilon}$ in it the mean value of the energy of the now degenerate system. If we again leave out of account the zero-point energy, we accordingly have, by (437):

$$\bar{\epsilon} = \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1} \quad . \qquad (444)$$

and, by (411):

$$\Delta = \frac{1}{N} \cdot e^{\frac{h\nu}{kT}} = \frac{1}{N} + \frac{h\nu}{\bar{\epsilon}} \quad . \quad . \quad . \quad . \qquad (445)$$

For $N = 1$ we get the earlier expression (443) for an individual oscillator. If we now allow N to increase at a definite temperature T the magnitude Δ of the relative mean square of the fluctuation decreases to an unlimited extent, as is to be expected. But in the case of the two components of Δ, the classical and the quantum terms, a characteristic difference manifests itself. When N increases the first decreases like $\frac{1}{N}$, that is, independently of the temperature; but the second term decreases like $\frac{1}{N} \cdot \left(e^{\frac{h\nu}{kT}} - 1\right)$. From this it follows that in order to make the energy fluctuation vanish N must be given a greater value as the temperature decreases. In other words, for every configuration, no matter how many oscillators it contains, there must be a range of temperature below which it cannot be cooled down, if a perfectly definite value of the energy of the configuration is to correspond to its temperature. Hence *for every system, no matter how great it may be, the concepts and laws of thermodynamics lose their validity if the temperature is appropriately lowered, and this occurs before the zero-point is reached*; and all thermodynamic reasoning based on a cooling of a definite system down to the absolute zero-point becomes void (cf. § 149 below).

§ 137. We have now covered the preliminary ground necessary to take up again—with a greater prospect of success—the energy distribution in the normal spectrum which we had to break off in § 114. As we there pointed out, this problem amounts to calculating the entropy and the other thermodynamic properties of pure cavity radiation. Having found that the microscopic consideration of a system furnishes us with the means of determining its entropy, we next undertake a microscopic investigation of pure cavity radiation, which we suppose enclosed in a volume of as simple and convenient a form as possible, namely in that of a cube whose length of edge is l. For the electromagnetic field equations referred to a vacuum

(IV, § 2) can be completely integrated in this case and so furnish the general solution of the problem from the microscopic point of view. To introduce the corresponding boundary conditions we assume the six sides of the hollow cube to be perfectly conducting (III, § 92) and consequently totally reflecting, and we have therefore to set the intensity components of the electric field tangential to a side equal to zero.

If we take the origin of co-ordinates at a corner of the cube a particular solution of the differential equations of the field is represented by the following expressions, where we pay due regard to the boundary conditions :

$$\left.\begin{aligned}
\boldsymbol{E}_x &= \cos\frac{a\pi x}{l}\cdot\sin\frac{b\pi y}{l}\cdot\sin\frac{c\pi z}{l}\cdot(e_1\cos 2\pi\nu t+e'_1\sin 2\pi\nu t)\\
\boldsymbol{E}_y &= \sin\frac{a\pi x}{l}\cdot\cos\frac{b\pi y}{l}\cdot\sin\frac{c\pi z}{l}\cdot(e_2\cos 2\pi\nu t+e'_2\sin 2\pi\nu t)\\
\boldsymbol{E}_z &= \sin\frac{a\pi x}{l}\cdot\sin\frac{b\pi y}{l}\cdot\cos\frac{c\pi z}{l}\cdot(e_3\cos 2\pi\nu t+e'_3\sin 2\pi\nu t)\\
\boldsymbol{H}_x &= \sin\frac{a\pi x}{l}\cdot\cos\frac{b\pi y}{l}\cdot\cos\frac{c\pi z}{l}\cdot(h_1\sin 2\pi\nu t-h'_1\cos 2\pi\nu t)\\
\boldsymbol{H}_y &= \cos\frac{a\pi x}{l}\cdot\sin\frac{b\pi y}{l}\cdot\cos\frac{c\pi z}{l}\cdot(h_2\sin 2\pi\nu t-h'_2\cos 2\pi\nu t)\\
\boldsymbol{H}_z &= \cos\frac{a\pi x}{l}\cdot\cos\frac{b\pi y}{l}\cdot\sin\frac{c\pi z}{l}\cdot(h_3\sin 2\pi\nu t-h'_3\cos 2\pi\nu t)
\end{aligned}\right\}\quad(446)$$

where a, b, c denote any three positive integers; for negative integers produce nothing new. The boundary conditions are satisfied in these expressions by the fact that the tangential components of the electric intensity of field $\boldsymbol{E}$ vanish for the six bounding faces $x=0$, $x=l$, $y=0$, $y=l$, $z=0$, $z=l$. It is easy for us to convince ourselves directly that the field equations (IV, § 2) are likewise all satisfied if certain relations exist between the constants which may all be summarized in one theorem as follows : if we denote a certain positive constant by a, the velocity of light by c, then there exist between the nine following quantities which we have arrayed in a square :

$$\begin{array}{ccc} \frac{ac}{2l\nu} & \frac{bc}{2l\nu} & \frac{cc}{2l\nu} \\[1ex] \frac{h_1}{a} & \frac{h_2}{a} & \frac{h_3}{a} \\[1ex] \frac{e_1}{a} & \frac{e_2}{a} & \frac{e_3}{a} \end{array}$$

all those relations which are fulfilled by the nine direction cosines of two orthogonal right-handed co-ordinate systems, that is, the cosines of the angles between each pair of axes of both systems (I, § 100).

Hence the sum of the squares of the members of each horizontal row or each vertical column is equal to 1, for example :

$$\frac{c^2}{4l^2\nu^2}(a^2 + b^2 + c^2) = 1 \quad . \qquad (447)$$

$$h_1^2 + h_2^2 + h_3^2 = a^2 = e_1^2 + e_2^2 + e_3^2.$$

Further the sum of the products of corresponding terms in each pair of parallel rows is equal to zero. Thus, for example :

$$\left.\begin{array}{r} ae_1 + be_2 + ce_3 = 0 \\ ah_1 + bh_2 + ch_3 = 0 \end{array}\right\} \quad . \qquad (448)$$

Finally relations of the form I (492) hold :

$$\frac{h_1}{a} = \frac{e_2}{a}\cdot\frac{cc}{2l\nu} - \frac{e_3}{a}\cdot\frac{bc}{2l\nu}$$

Thus :

$$h_1 = \frac{c}{2l\nu}(ce_2 - be_3) \quad . \quad . \qquad (449)$$

and so forth.

If any values are given to the integers a, b, c, then by (447) the vibration number ν is determined. This means that of the six quantities e_1, e_2, e_3, h_1, h_2, h_3 only two can be chosen arbitrarily; the others are then uniquely derived from them in a linear and homogeneous form. If, for example, we give e_1 and e_2 any arbitrary values then e_3 can be calculated from (448), and the values of h_1, h_2, h_3 follow from the relations of the form (449). The same relations hold between the accented constants e'_1, e'_2, e'_3, h'_1, h'_2, h'_3 as hold between the unaccented constants, the two sets of constants being otherwise quite independent of each other. Hence two terms of the accented system can also be arbitrarily chosen, so that of all the constants that occur in the above equations four constants still remain undetermined when a, b and c are given.

Now if for each triplet of numbers a, b, c we form expressions of the form (446) and sum up the corresponding field components, we again obtain a solution of the field equations, which, however, is now sufficiently general to represent any possible arbitrary radiation whatsoever in the hollow cube in question and in fact, in a unique form. To prove this let us consider the initial state of the electromagnetic field. If we set $t = 0$, we get for the general initial state, from (446):

$$E_x = \Sigma e_1 \cos \frac{a\pi x}{l} \cdot \sin \frac{b\pi y}{l} \cdot \sin \frac{c\pi z}{l}$$

$$E_y = \Sigma e_2 \sin \frac{a\pi x}{l} \cdot \cos \frac{b\pi y}{l} \cdot \sin \frac{c\pi z}{l}$$

$$E_z = \Sigma e_3 \sin \frac{a\pi x}{l} \cdot \sin \frac{b\pi y}{l} \cdot \cos \frac{c\pi z}{l}$$

$$H_x = -\Sigma h'_1 \sin \frac{a\pi x}{l} \cdot \cos \frac{b\pi y}{l} \cdot \cos \frac{c\pi z}{l}$$

$$H_y = -\Sigma h'_2 \cos \frac{a\pi x}{l} \cdot \sin \frac{b\pi y}{l} \cdot \cos \frac{c\pi z}{l}$$

$$H_z = -\Sigma h'_3 \cos \frac{a\pi x}{l} \cdot \cos \frac{b\pi y}{l} \cdot \sin \frac{c\pi z}{l}$$

where the summation is to be performed over all the numbers a, b, c from 1 to ∞. Now if the vectors E and H are given for $t = 0$ in any way, but of course so that $\operatorname{div} E = 0$ and $\operatorname{div} H = 0$ and so that the boundary conditions are fulfilled, the above sums represent the Fourier expansions of the functions E and H; the coefficients of these expansions are, as we know, uniquely determined (cf. II, § 39) and can be calculated by simple rules. This then determines the course of events for all values of the time t.

Now if we wish to apply the solution just found to heat radiation, we must, after what has been said in § 94, assume the length of the edge of the cube l to be very great compared with the wave-lengths $\lambda = \frac{c}{\nu}$; from this it follows by (447) that $a^2 + b^2 + c^2$ is very great. Starting from this result, we can easily calculate how many different triplets of numbers a, b, c give a vibration number which lies within the narrow spectral interval between ν and $\nu + \Delta\nu$. For by (447) these are obviously characterized by the condition :

$$\left(\frac{2l\nu}{c}\right)^2 < a^2 + b^2 + c^2 < \left(\frac{2l(\nu + \Delta\nu)}{c}\right)^2. \quad . \quad (450)$$

If we now depict every triplet of numbers a, b, c by means of a geometrical point by regarding the values of the positive integers a, b, c as co-ordinates in a rectangular system of co-ordinates, the points so obtained fill an octant of infinite space, and the condition (450) states that the distance of one of these points from the origin of co-ordinates lies between the values $\frac{2l\nu}{c}$ and $\frac{2l(\nu + \Delta\nu)}{c}$. The required number is therefore equal to the number of points which lie between the two octants of the spherical surfaces that correspond to radii of the values just mentioned. Since a cube of volume 1 corresponds to every point, this number is simply equal to the volume of the thin spherical shell, that is, to :

$$\frac{1}{8} \cdot 4\pi \cdot \left(\frac{2l\nu}{c}\right)^2 \cdot \frac{2l\Delta\nu}{c} = \frac{4\pi l^3 \nu^2 \,.\, \Delta\nu}{c^3} \quad . \qquad (451)$$

No matter how small the frequency interval $\Delta\nu$ may be assumed to be, we can nevertheless choose l sufficiently great to make this number have a very great value.

§ 138. Now that we have succeeded by microscopic considerations in dividing the most general process of monochromatic radiation that can take place in the assumed cavity into a great but definite number of mutually independent simply periodic vibrations of the same frequency it suggests itself readily to us to compare its thermodynamic probability with that of a system of like but mutually independent simply periodic oscillators of the same frequency such as have been investigated in the preceding sections. For the question as to whether the vibrations are of an electromagnetic or a mechanical nature cannot affect the probability. The only essential condition is that the microscopic events in the two systems shall correspond uniquely, that is, that a definite state of the system of oscillators shall be assigned to each state of the cavity radiation and conversely. For if this condition is fulfilled the number of microscopic states that correspond to a definite macroscopic state does not depend on whether the system of oscillators or the cavity radiation is used in the discussion.

But another point is also to be considered. According to the preceding paragraph the state of radiation for a definite frequency ν is determined by four mutually independent constants, whereas the state of vibration of an oscillator with a single degree of freedom contains, by (430), only two independent constants. From this we must infer that *two* degrees of freedom belong to radiation of frequency ν, and that therefore a definite state of two mutually independent operators corresponds to every state of radiation of this frequency, and conversely. Hence the processes of monochromatic radiation in the cavity in question are by (451) statistically equivalent to the vibrations of :

$$N = 2 \cdot \frac{4\pi l^3 \nu^2 \Delta\nu}{c^3} \quad . \tag{452}$$

simply periodic oscillators with a single degree of freedom, and their energy is given for a definite temperature T by

(437). If we also consider that the zero-point energy of the radiation vanishes, by (330), we get for the energy of the monochromatic cavity radiation in question :

$$E = \frac{8\pi h\nu^3\Delta\nu \cdot l^3}{c^3} \cdot \left(e^{\frac{h\nu}{kT}} - 1\right)^{-1} \quad . \quad (453)$$

and, dividing by the volume l^3 of the hollow cube, we get for the spatial density of this energy :

$$\frac{8\pi h\nu^3\Delta\nu}{c^3} \cdot \left(e^{\frac{h\nu}{kT}} - 1\right)^{-1} = \mathfrak{u}_\nu . \varDelta_\nu \quad (454)$$

where we use the notation already introduced in (296). From this it follows by (297) that the specific intensity of the linearly polarized radiation in any direction is :

$$K_\nu = \frac{c \,.\, \mathfrak{u}_\nu}{8\pi} = \frac{h\nu^3}{c^2} \cdot \left(e^{\frac{h\nu}{kT}} - 1\right)^{-1} \quad . \quad (455)$$

which represents the required law of radiation. If we compare it with (360) we see that it agrees exactly with Wien's Displacement Law.

From (436) and (452) we obtain for the characteristic function $\varPsi$ of the monochromatic radiation in the volume V :

$$\varPsi = -\frac{8\pi k\nu^2\Delta\nu \,.\, V}{c^3} \log\left(1 - e^{-\frac{h\nu}{kT}}\right) \quad . \quad . \quad (456)$$

If we refer the specific intensity of radiation to the wave-length λ instead of to the frequency ν, we obtain from (363) and (455) :

$$E_\lambda = \frac{c^2 h}{\lambda^5}\left(e^{\frac{ch}{k\lambda T}} - 1\right)^{-1} = \frac{c_1}{\lambda^5}\left(e^{\frac{c_2}{\lambda T}} - 1\right)^{-1} \quad . \quad (457)$$

as the specific intensity of a monochromatic linearly polarized beam of wave-length λ radiated by a black body at the temperature T into empty space.

§ 139. For *large* values of λT ($\gg c_2$) the expression (457) merges into the equation :

$$E_\lambda = \frac{ckT}{\lambda^4} \quad . \quad . \quad . \quad (458)$$

In the same way (455) becomes:

$$K_\nu = \frac{k\nu^2 T}{c^2} \quad . \quad . \quad . \qquad (459)$$

which is Rayleigh's Law of Radiation. The same law results if at any arbitrary temperature T we assume the quantum of action h to become infinitely small. Thus, by § 134, it represents the "classical" law of radiation. The fact that this law is contrary to experimental results and that therefore the classical theory is not generally valid is simply seen by observing that the expression $K_\nu . d_\nu$ when integrated from $\nu = 0$ to $\nu = \infty$ becomes infinitely great by (459).

For *small* values of $\lambda T (\ll c_2)$, on the other hand, we get from (457) that:

$$E_\lambda = \frac{c_1}{\lambda^5} \cdot e^{-\frac{c_2}{\lambda T}} \quad . \qquad (460)$$

This equation expresses Wien's Law of Energy Distribution, which has been proved to be very successful in the optical region but fails at high temperatures, because E_λ actually increases beyond all limits when the temperature increases to an unlimited extent, which is not the case in (460). According to the most accurate measurements the value of the constant $c_2 = \frac{ch}{k}$ is:

$$c_2 = \frac{ch}{k} = 1{\cdot}430 \text{ cm.} \times \text{degree} \qquad (461)$$

§ 140. The spatial total density u of cavity radiation at the temperature T is given by (454) as:

$$u = \int_0^\infty \mathfrak{u} \,.\, d\nu = \frac{8\pi h}{c^3}\int_0^\infty \nu^3 \left(e^{\frac{h\nu}{kT}} - 1\right)^{-1} \cdot d\nu$$

$$= \frac{8\pi h}{c^3}\int_0^\infty \left(e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} + \cdot \cdot \cdot\right)\nu^3 d\nu$$

and by integrating each member in turn we get:

$$u = \frac{48\pi h}{c^3}\left(\frac{kT}{h}\right)^4 \cdot \frac{\pi^4}{90} \quad . \quad . \quad . \qquad (462)$$

where we have used the result :

$$1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \cdots = \frac{\pi^4}{90} = 1{\cdot}0823 \; . \qquad (463)$$

This is the Stefan–Boltzmann Law (326) or (328), in which the constant now has the value :

$$a = \frac{8\pi^5 k^4}{15c^3h^3} \text{ or } \sigma = \frac{2\pi^5 k^4}{15c^2h^3} \; . \qquad (464)$$

§ 141. With the help of the measured values of σ and c_2 we can now easily calculate the universal constants h and k. For it follows from the equations (461) and (464) that :

$$h = \frac{15\sigma c_2^4}{2\pi^5 c^2}\,, \quad k = \frac{15\sigma c_2^3}{2\pi^5 c} \; . \qquad (465)$$

With the values given for the constants σ in (331) and c_2 in (461) we get :

$$\left.\begin{aligned} h &= 6{\cdot}55 \,.\, 10^{-27} \text{ erg sec.} \\ k &= 1{\cdot}373 \,.\, 10^{-16} \text{ erg/degree} \end{aligned}\right\} . \qquad (466)$$

From equation (457) we get for the wave-length λ_m, to which the maximum of the radiated intensity E_λ corresponds in the spectrum of black body radiation :

$$\left(\frac{dE_\lambda}{d\lambda}\right)_{\lambda = \lambda_m} = 0.$$

Differentiation gives :

$$e^{-\beta} + \frac{\beta}{5} - 1 = 0$$

where, for brevity, we have set :

$$\frac{ch}{k\lambda_m T} = \beta.$$

The root of this transcendental equation is :

$$\beta = 4{\cdot}9651.$$

Accordingly, $\lambda_m T = \frac{ch}{\beta k} = \frac{c_2}{\beta}$, that is, constant, as is demanded by Wien's Displacement Law (365). The value of the constant b comes out as :

$$b = \frac{c_2}{\beta} = \frac{1{\cdot}430}{4{\cdot}9651} = 0{\cdot}288$$

which agrees with the measured value (366).

§ 142. Our calculation of the energy distribution in the normal spectrum was built up only on the statistical definition of entropy. It was independent of any assumption whatsoever about the nature of the processes by which cavity radiation of any arbitrary distribution of energy is transformed into normal cavity radiation. But, as we have already had occasion to emphasize repeatedly in § 105 and § 125, it is obvious that in nature such processes, which act as coupling agencies between the energies of different spectral regions, must be active in promoting normal energy distribution, and it is important to enquire what sort of coupling nature actually makes use of in the present case. Everything of course depends on gaining a closer insight into the acts of emission and absorption of radiation.

The atomic model proposed by Bohr certainly approaches reality most closely. This model is an oscillator which can have a number of discrete energy-values $\epsilon_0 < \epsilon_1 < \epsilon_2 \ldots < \epsilon_n < \ldots$, as in § 122. If such an atom is situated in a field of radiation the absorption of radiant energy takes place by the abrupt transition of the atom from a state of lesser energy ϵ_n to a state of greater energy ϵ_p; the emission of radiant energy is carried out by a transition in the reverse direction. In this process the absorbed or emitted energy, respectively, is always monochromatic, and its frequency ν is related to the abrupt change in the energy of the atom as follows :

$$h\nu = \epsilon_p - \epsilon_n \quad . \quad . \quad . \quad . \quad . \quad (467)$$

Hence the amount of transformed radiant energy is always equal to $h\nu$, a so-called *light-quantum* or *photon*.

The stationary state in this exchange of energy between atomic energy and radiant energy is characterized by the fact that over a very long time the transition of the atomic energy from ϵ_n to ϵ_p occurs just as often as the opposite transition from ϵ_p to ϵ_n. But we have here to take into account the fact that during this time the atom finds itself, by § 126, more often in the state with lesser energy ϵ_n than in that with greater energy ϵ_p. For, by (407), the corresponding numbers denoting these frequencies of occurrence are :

$$w_n = \frac{e^{-\frac{\epsilon_n}{kT}}}{\Sigma e^{-\frac{\epsilon_n}{kT}}} \text{ and } w_p = \frac{e^{-\frac{\epsilon_p}{kT}}}{\Sigma e^{-\frac{\epsilon_p}{kT}}} \quad . \quad . \quad (467a)$$

Thus on the average the atom remains longer in the one state than in the other. Now to represent the frequency of transition of the atomic energy from ϵ_n to ϵ_p and conversely, Einstein has introduced some very plausible assumptions which bring us to our goal by means of a simple calculation. He assumes that the frequency with which absorption occurs, that is, the transition from ϵ_n to ϵ_p, is firstly proportional to the frequency number w_n, and secondly to the intensity of radiation which strikes the atom and which has the frequency ν determined by (467), that is, equal to $\alpha K_\nu w_n$. In the same way the frequency with which the opposite transition occurs, the act of emission, is equal to $\alpha K_\nu w_p$. But besides the so-called " induced " emission caused by the incident radiation there is also a so-called " spontaneous " emission which is quite independent of the external field of radiation and its frequency is expressed simply by βw_p. Here β like α is a certain factor of proportionality which is independent of the temperature. The condition for the stationary state runs :

$$\alpha K_\nu w_n = \alpha K_\nu w_p + \beta w_p$$

and in view of (467) and (467a) it follows from this that :

$$K_\nu = \frac{\beta}{\alpha}\left(e^{\frac{h\nu}{kT}} - 1\right)^{-1}$$

in agreement with (455).

Of course, in establishing the above condition of stability we may just as well, and perhaps more "picturesquely," use the concept of "frequency" in a spatial sense, referring to the simultaneous state of a great number of similarly constituted atoms instead of in the time sense, referring to a single atom.

CHAPTER V

EQUATION OF STATE OF MATERIAL BODIES. CHEMICAL CONSTANT. NERNST'S HEAT THEOREM

§ 143. THE most general and the most direct way of arriving at the equation of state of any given material body consists, as we have seen in Chapter II, in calculating the sum of the states by (419) and from it, by (420), the characteristic function of the body. We shall first carry out this process for a *gas* which consists of N similar monatomic molecules and which occupies a given volume V.

Our first step is to calculate the sum of the states. For the sake of simplicity we shall assume that the gas is in an ideal state, that is, that the energy of the gas reduces itself essentially to the kinetic energy of the molecules. Since the molecules are all of the same kind, it suggests itself to us to treat the gas according to § 122 as a group of N similar elementary systems isolated from one another, these systems being the molecules, and accordingly to apply the formulæ (404) and (402) for the sum of the states of an elementary system and the characteristic function of the total system; this is founded on the fact that every individual molecule can possess every value of the energy and can occupy any place in the volume V. But closer inspection reveals that this procedure is inadmissible. For the formulæ quoted hold only for the case where the elementary systems are isolated from one another. In deriving them we assumed that for every distribution of states among the elementary systems there is a particular microscopic state; that is, that if two elementary systems exchange their states a new microscopic state of the total system results. But in the case of similar molecules of a gas this assumption no longer holds. For if two similar molecules of a gas exchange their states, that is their positions and their velocities, the microscopic state of the gas remains unchanged; it is distinguished in no way from the preceding microscopic state, and does not therefore require to receive special consideration again when the statistical weight is being calculated. In spite of this antithesis in the primary conditions the procedure above suggested has frequently been applied and the error incurred has expressed itself in a difficulty for which the whole theory has unjustifiably been held responsible.

We shall avoid committing this error and shall therefore encounter no such difficulty. Accordingly we do not regard our gas, in the sense of § 122, as a group of many similar isolated elementary systems, namely molecules, but in the sense of § 127 as a single elementary system having a certain number of degrees of freedom so that, corresponding to a definite temperature, there is a perfectly definite value for energy. Then the expressions (419) and (420) hold for the sum of the states Z and the characteristic function Ψ of the gas.

To calculate the sum of the states Z we must take into consideration all the different possible microscopic states of the gas and substitute the values of their energies in (419). This requires us to set up an hypothesis about the constitution of the gas, on the basis of which we can derive the possible microscopic states; that is, we can quantise. Several such hypotheses have been put forward in the course of time; they naturally lead to different results. But there is a very wide range over which the results agree with one another; it is the only range which has so far been accessible to direct measurement, since the cases that can be realized physically all fall within this range. It is characterized by the fact that in the phase-space of the gas the size of an elementary system (427) is very small compared with the size of the whole region in question. We shall see below, in (475), how this condition expresses itself in physically measurable quantities. If we assume it to be fulfilled we can write every individual term in the sum of the states as a differential by multiplying it according to (427) by :

$$1 = \frac{1}{h^f} \cdot d\tau \quad . \tag{468}$$

Further, the sum of the states (419) :

$$Z = \sum_{z} e^{-\frac{E_n}{kT}} \quad . \tag{469}$$

becomes a phase integral which is to be taken over the whole phase-space of the gas.

Since each of the N monatomic molecules moving freely in space has three degrees of freedom, $f = 3N$; and the differential element of space becomes, by (422) :

$$d\tau = dq_1 \,.\, dp_1 \,.\, dq_2 \,.\, dp_2 \,.\, \ldots \, dq_{3N} \,.\, dp_{3N} \quad . \tag{470}$$

where $q_1, q_2 \ldots q_{3N}$ denote the $3N$ rectangular co-ordinates of the N molecules, and $p_1, p_2 \ldots p_{3N}$ denote the corresponding momentum co-ordinates; so that the energy of the gas is :

$$E = \frac{1}{2m}(p_1^2 + p_2^2 + \ldots p_{3N}^2) + E_0 \,. \tag{471}$$

where E_0 is used to designate the zero-point energy, that is, the internal energy of the gas molecules.

The integration is to be performed over all the different microscopic states of the gas, each microscopic state being counted once. Now if we integrate for every molecule over all the values of its co-ordinates which are permissible within the given volume and over all the momentum components from $-\infty$ to $+\infty$ we do not obtain the microscopic state of the gas once but just as often in number as there are permutations between N molecules, namely $N!$ times. For since the molecules are all similar, every permutation of the co-ordinates and momenta gives a new integration term but no new microscopic state. Accordingly the expression for the sum of the states runs, according to (469), if we take into account (468) and (470):

$$Z = \frac{1}{h^{3N}N!}\int e^{-\frac{E}{kT}} . dq_1 . dp_1 \;.\;.\;.\; dq_{3N} . dp_{3N} \,. \tag{472}$$

where the integration is now to be taken for every molecule over all the points within V and over all the momenta from $-\infty$ to $+\infty$. Substituting the value (471) for E and performing the integration over the $3N$ point coordinates q, we get, using Stirling's formula (386):

$$Z = \left\{\frac{eV}{h^3N}\iiint\limits_{-\infty}^{+\infty} e^{-\frac{p_1^2+p_2^2+p_3^2}{2mkT}}\, dp_1\, dp_2\, dp_3\right\}^N . e^{-\frac{E_0}{kT}}$$

Here the triple integral is equal to $(2\pi mkT)^{\frac{3}{2}}$, consequently:

$$Z = \left\{\frac{eV}{h^3N} \cdot (2\pi mkT)^{\frac{3}{2}}\right\}^N . e^{-\frac{E_0}{kT}} \,. \tag{473}$$

and by (420):

$$\Psi = kN \log\left\{\frac{eV}{h^3N}(2\pi mkT)^{\frac{3}{2}}\right\} - \frac{E_0}{T} . \tag{474}$$

This last equation expresses all the thermodynamic properties of the gas.

The expression Ψ also gives us information about the physical meaning of the condition which we introduced by means of (468) and which states that h may be treated as an infinitely small quantity. For we must have:

$$\frac{V(mkT)^{\frac{3}{2}}}{Nh^3} \gg 1 \,. \tag{475}$$

According to this the product of the atomic volume $\frac{V}{N}$ and the cube of $\sqrt{T}$ must not fall below a certain order of magnitude, which depends on the nature of the gas, if the formula (474) is still to remain applicable. If this condition is transgressed, more complicated relationships replace the ordinary gas laws; these relationships are sometimes called degenerate, but here the word degenerate is to be interpreted in quite a different way from that of § 127. This phenomenon of gas degeneracy is entirely foreign to classical theory, since the condition (475) is always fulfilled for an infinitely small value of h. So gas degeneracy corresponds to the deviation of the law of radiation (457) from Rayleigh's Classical Law of Radiation (458). But it is to be noted that an essential difference exists in that although the classical theory leads to Rayleigh's Law of Radiation it does not lead to the expression (474) of the characteristic function of an ideal gas. For in classical theory the value of the infinitely small constant h remains quite indeterminate (cf. § 133 above). It is only the introduction of the quantum theory that leads to an absolute value of the entropy and the characteristic function. Concerning the significance of this circumstance see § 150 below.

§ 144. We shall now derive the thermodynamic properties of the gas under consideration from the expression (474) found for Ψ. By (115) we obtain for the pressure:

$$p = T \cdot \frac{\partial \Psi}{\partial V} = \frac{kNT}{V} . \qquad (476)$$

If we compare this equation with the equation of state of the ideal gas (96) we see that there is complete agreement if $kN = Rn$ or:

$$\frac{k}{R} = \frac{n}{N} . \qquad (477)$$

That is, the universal gas constant k is nothing else than the absolute gas constant in the equation of state, referred to molecules and not to moles. Substituting the numerical values (466) and (55) we get:

$$\frac{n}{N} = 1{\cdot}65 \,.\, 10^{-24} \qquad . \qquad (478)$$

as the ratio of the number of moles to the number of molecules, or, what amounts to the same, of the molecular mass to the molar mass (Avogadro's number).

According to this the elementary charge of electricity, that is, the charge of an electron or of a univalent ion in electrostatic units is, by III, § 66 :

$$2{\cdot}895 \,.\, 10^{14} \,.\, 1{\cdot}65 \,.\, 10^{-24} = 4{\cdot}78 \,.\, 10^{-10}$$

which agrees with the measurements of R. A. Millikan.

Further, we obtain from (405) for the energy of the gas :

$$E = T^2 \cdot \frac{\partial \Psi}{\partial T} = \frac{3}{2} kNT + E_0 \,. \qquad (479)$$

That is, for the molecular heat at constant volume we have $\frac{3k}{2}$; and for the molar heat at constant volume $\frac{3R}{2}$, which, measured in calories, is about equal to 3, according to (57). This agrees with the values given in § 31 for a monatomic gas.

Finally, the entropy of the gas is, by (406) :

$$S = \Psi + T \frac{\partial \Psi}{\partial T} = kN \log \left\{ \frac{e^{\frac{5}{2}} V}{h^3 N} \cdot (2\pi mkT)^{\frac{3}{2}} \right\} . \qquad (480)$$

which agrees with (109), except that here, too, the indefinite additive constant of the classical theory is replaced by a perfectly definite quantity.

§ 145. Whereas the energy fluctuations of the whole gas at a definite temperature are only extremely small each individual molecule undergoes considerable fluctuations in its energy, and so also in its velocity. The law governing these fluctuations results from the formula (415) for the energy fluctuations of a system of arbitrary degeneracy, which is immersed in a heat-bath of definite temperature. Here ϵ_n denotes any possible amount of energy of the molecule, thus :

$$\epsilon_n = \frac{p^2}{2m} + \epsilon_0 \quad . \qquad (481)$$

where p denotes the total momentum $\sqrt{p_1{}^2 + p_2{}^2 + p_3{}^2}$, ϵ_0 the internal energy of the molecule, and g_n is the number of microscopic states of the molecule that correspond to the energy interval between ϵ_n and $\epsilon_n + d\epsilon_n$:

$$g_n = \frac{1}{h^3} \int dq_1 \, dq_2 \, dq_3 \, dp_1 \, dp_2 \, dp_3,$$

where the integration is to be performed with respect to the three momentum components over the infinitely small region between p and $p + dp$; thus :

$$\int dp_1 \, dp_2 \, dp_3 = 4\pi p^2 \, dp.$$

Since the value of (415) does not depend on a constant factor in g_n, we get :

$$w_n = p^2 dp \, . \, e^{-\frac{\epsilon_n}{kT}} \left(\int_0^\infty e^{-\frac{\epsilon_n}{kT}} . \, p^2 dp \right)^{-1}$$

If we integrate, taking into account (481) and omitting the index n which now becomes superfluous, we get :

$$w = \sqrt{\frac{2}{\pi}} \cdot \frac{1}{(mkT)^{\frac{3}{2}}} \cdot e^{-\frac{p^2}{2mkT}} \, p^2 dp \quad . \quad . \quad (482)$$

or, if we introduce the velocity v by writing the momentum $p = mv$ we get :

$$w = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \cdot e^{-\frac{mv^2}{2kT}} \cdot v^2 dv \quad . \quad . \quad (483)$$

as the probability that the molecule will at any instant have a velocity between v and $v + dv$. Of course, this expression also gives a measure of the number of times that the velocity v occurs simultaneously in a great number of molecules of a gas at temperature T (Maxwell's Law of the Distribution of Velocities). It is to be observed that m and k occur only in the form of their ratio, so that the probability law (483) remains correct if we calculate with moles instead of with molecules.

§ 146. If the N molecules of the gas are not all of the same kind, but sub-divide into different types 1, 2, 3, . . ., so that :

$$N_1 + N_2 + N_3 + \ldots = N \quad . \quad . \quad (484)$$

the expression for the characteristic function becomes correspondingly more general: this modification is effected by making the calculation according to the same method as was used above in § 143. In forming the sum of the states Z we then have in place of the equation (468) the following:

$$1 = \frac{1}{h^f} d\tau_1 d\tau_2 d\tau_3 \quad . \ . \ .$$

where the number of degrees of freedom of the system is now:

$$f = 3N_1 + 3N_2 + 3N_3 + \quad . \ . \ .$$

and $d\tau_1$, $d\tau_2$, . . . denote the elementary systems of the phase-spaces corresponding to the different kinds of gases. The exponential function having the energy E in the exponent sub-divides by (471) into the product of the exponential functions referring to the individual kinds of gases, and the integrations over the elementary regions are performed in exactly the same way as above. Finally the number of permutations $N!$ in the denominator of the sum of the states is replaced by the smaller product $N_1!\ N_2!\ N_3!$. . . . . For the microscopic state of the gas remains unchanged only when *similar* molecules are permuted among themselves.

We thus obtain as a result of the calculation the following characteristic function of the gaseous mixture:

$$\Psi = \sum_{1,2,\dots} kN_1 \log \left\{ \frac{eV}{h^3 N_1} (2\pi m_1 kT)^{\frac{3}{2}} \right\} - \frac{E_0}{T} \quad . \quad . \qquad (485)$$

where the summation refers to the individual kinds of molecules. This expression is analogous to (474). We obtain for the energy:

$$E = \frac{3}{2} k(N_1 + N_2 + \ \cdot \ \cdot \ \cdot \ )T + E_0 \ . \quad . \qquad (486)$$

which is analogous to (479); and for the entropy:

$$S = \sum_{1,2,\dots} kN_1 \log \left\{ \frac{e^{\frac{5}{2}} V}{h^3 N_1} (2\pi m_1 kT)^{\frac{3}{2}} \right\} \ . \qquad (487)$$

which is analogous to (480).

Comparison with (170) again shows the complete agreement of these formulæ with those of general thermodynamics, except that here there is no indefiniteness, not even in the additive constants a_1, a_2, a_3. . . . Thus the additive constant is a definite quantity which is characteristic of the gas. It is called the "chemical constant" of the gas.

§ 147. As a further example let us now calculate the characteristic function of a *solid body* consisting of N atoms supposed similar for the present. As regards the constitution of the body we shall assume that the atoms, or at least the very great majority of them, are subject to quasi-elastic forces. The energy of the body is then of the form :

$$E = U + K + E_0 \quad . \quad . \quad . \quad . \qquad (488)$$

where U, the potential energy, is a homogeneous quadratic function of the components of the relative displacements of the N atoms ; K is the kinetic energy, a purely quadratic function of the $3N$ velocity components, and E_0 is the zero-point energy.

By introducing $3N$ suitably chosen homogeneous linear functions q_1, q_2, . . . q_{3N} of the displacement components we can always arrange so that the two functions U and K, expressed in terms of the co-ordinates q and their derivatives $\dot{q}$, become purely quadratic and that therefore the dependence of the energy on the co-ordinates q and the momenta p can be represented in the form :

$$E = a_1 q_1^2 + b_1 p_1^2 + a_2 q_2^2 + b_2 p_2^2 + \cdot \cdot \cdot + E_0 \; . \qquad (489)$$

The motions of the N atoms can thus be reduced to the superposition of the vibrations of $3N$ independent linear oscillators of the same kind as those considered in § 135. A particular solution of the equations of motion is obtained, for example, if all the components q and p are set equal to zero except one, say q_i and p_i. Then all the atoms of the body vibrate with the same period, which is determined by constants a_i and b_i, and in the same phase, since all the displacement components are proportional to the one co-ordinate q_i. In other words, the most general motion of the N atoms of the body may be regarded as composed of $3N$ simply periodic stationary vibrations of the whole atomic complex. The slow vibrations correspond to the elastic or acoustic spectrum, the rapid vibrations to the thermal spectrum. So we here have a spectral resolution similar to that which occurs in cavity radiation. Yet there is an essential difference, firstly in the occurrence of the zero-point energy E_0, which cannot be left out of account in a material body, and secondly in the fact that the spectrum of the cavity radiation stretches to infinity, whereas in the spectrum of the atomic vibrations only $3N$ vibration periods occur.

From (419) we obtain for the sum of the states of the body :

$$Z = \sum_z e^{-\frac{E}{kT}}$$

If we here substitute the value of E from (489), Z is represented as the product of the sums of the states of the whole $3N$ oscillators, multiplied by a constant factor due to the zero-point energy; that is, by (435) :

$$Z = e^{-\frac{E_0}{kT}}\left(1 - e^{-\frac{h\nu_1}{kT}}\right)^{-1} \cdot \left(1 - e^{-\frac{h\nu_2}{kT}}\right)^{-1} \dots \quad (490)$$

We must here interpose a remark. The fact that every body sends out vapour into neighbouring space shows that in reality the atoms do not all act on one another with quasi-elastic forces, but rather that there are certainly some among them which move progressively forwards. These " vagabond " or " loosely bound " atoms will not, however, always be the same ones; rather there will be a kind of continual exchange between them and the " localized " or " tightly bound " atoms. A consequence of this is that after a fair length of time the atoms of the body will partly or totally have changed their places, and the question arises whether this circumstance will not correspondingly increase the possible microscopic states of the body. If we take into account, however, that the atoms are all of the same kind it follows, just as above in the case of a gas, that no new microscopic state is produced by a permutation of the atoms and that therefore the expression (490) for the sum of the states will also remain unchanged when we take into account the process of exchange among the atoms. By (420) we get from (490) as the characteristic function of the body :

$$\Psi = -\frac{E_0}{T} - k\sum_{i=1}^{i=3N} \log\left(1 - e^{-\frac{h\nu_i}{kT}}\right). \tag{491}$$

If we denote the number of vibration frequencies ν_i that lie in the interval between ν and $\nu + d\nu$ by $f(\nu)d\nu$, so that :

$$\int_0^\infty f(\nu)\,d\nu = 3N \tag{492}$$

then :

$$\Psi = -\frac{E_0}{T} - k\int_0^\infty f(\nu)\cdot\log\left(1 - e^{-\frac{h\nu}{kT}}\right)d\nu\quad . \tag{493}$$

It now remains for us to determine the function $f(\nu)$. So long as ν is fairly small, that is, for long waves, we shall obtain an approximate value for $f(\nu)$ if we assume the matter in the body to be continuously distributed. With this assumption an approximate value for the required number can be derived from a comparison with the spectrum of cavity radiation treated above. For in equation (452), § 138, we found for the electromagnetic vibrations in an evacuated cavity space of volume $V = l^3$ the following value for the number of vibrations, each of one degree of freedom, that lie in the frequency interval ν and $\nu + d\nu$:

$$\frac{8\pi V\nu^2 d\nu}{c^3}\quad . \quad . \quad . \quad . \quad . \quad . \tag{494}$$

If we take into consideration the fact that in electromagnetic radiation only transverse vibrations, in mechanical vibrations transverse *and* longitudinal vibrations occur, and that the number of the latter is half as great as that of the former for every direction of propagation, it is clear that in the present case the number (494) must be increased by half its value, so that we obtain :

$$\frac{12\pi V\nu^2 d\nu}{q^3} = f(\nu)d\nu \quad . \qquad (495)$$

as the number of vibrations, each of one degree of freedom, which belong to the interval between ν and $\nu + d\nu$. Here q denotes a certain mean value for the velocity of propagation of elastic waves in the substance of the body.

For greater values of ν (495) of course loses its validity, since, on account of (492), the function $f(\nu)$ must rapidly converge to zero as ν increases. But according to Debye we obtain a very good approximate value if we regard the formula (495) as exactly valid up to a certain frequency ν_1, thus :

$$\left.\begin{array}{r} \text{for } \nu < \nu_1 \text{ we set } f(\nu) = \dfrac{12\pi V\nu^2}{q^3} \\ \text{but for } \nu > \nu_1 \text{ we set } f(\nu) = 0 \end{array}\right\} \quad . \quad . \qquad (496)$$

Moreover, we are encouraged to make this assumption because at low temperatures the higher frequencies exert no influence at all on the value of the integral in (491), whereas at high temperatures the classical law of the equipartition of energy retains its validity, as in (439), in which the form of $f(\nu)$ is of no importance, since we are concerned only with the total number of the degrees of freedom.

The condition (492) serves to determine the limiting frequency ν_1. Combined with (496) this gives :

$$\int_0^{\nu_1} \frac{12\pi V\nu^2}{q^3} d\nu = 3N.$$

Consequently :

$$\nu_1 = q\sqrt[3]{\frac{3N}{4\pi V}} \quad . \quad . \qquad (497)$$

If this value is inserted as the upper limit of the integral in (493) and if we transform the integration variable by means of :

$$x = \frac{h\nu}{kT}$$

and use the abbreviation :

$$\Theta = \frac{h\nu_1}{k} = \frac{hq}{k} \cdot \sqrt[3]{\frac{3N}{4\pi V}} \quad . \tag{498}$$

we get as the expression for the characteristic function :

$$\Psi = -\frac{E_0}{T} - \frac{9NkT^3}{\Theta^3} \int_0^{\frac{\Theta}{T}} x^2 \log(1 - e^{-x}) dx \ . \tag{499}$$

Using (499) we get the entropy S from (406), the energy E from (405) and the pressure p as a function of the temperature T and the volume V from (115). In calculating p we must note that not only Θ but also E_0 depends on the volume V.

§ 148. For high temperatures ($T \gg \Theta$) only small values of the variable of integration x come into question. Hence we may write in the integral :

$$\log(1 - e^{-x}) = \log x$$

and if we then perform the integration we get for the characteristic function :

$$\Psi = -\frac{E_0}{T} + 3Nk \log \frac{e^{\frac{1}{3}} T}{\Theta} \quad . \tag{500}$$

and for the energy :

$$E = T^2 \frac{\partial \Psi}{\partial T} = E_0 + 3NkT \ . \quad . \tag{501}$$

while the entropy comes out as :

$$S = \Psi + \frac{E}{T} = 3Nk \log \frac{e^{\frac{4}{3}} T}{\Theta} \ . \tag{502}$$

From (501) we get for the atomic heat of a solid body at constant volume, corresponding to the empirical law of Dulong and Petit :

$$c_v = \frac{1}{N} \frac{\partial E}{\partial T} = 3k \tag{503}$$

a value which is twice as great as the atomic heat given in (479) for a monatomic gas.

For *low* temperatures ($T \ll \Theta$) the upper limit of the integral in (499) becomes infinitely great and we get by repeated integration by parts:

$$\int_0^\infty x^2 \log (1 - e^{-x}) dx = -\frac{1}{3}\int_0^\infty \frac{x^3 dx}{e^x - 1} = -\frac{\pi^4}{45}.$$

Hence we get the characteristic function:

$$\varPsi = -\frac{E_0}{T} + \frac{\pi^4 NkT^3}{5\Theta^3} \quad . \quad . \quad . \quad (504)$$

and the energy:

$$E = T^2 \frac{\partial \varPsi}{\partial T} = E_0 + \frac{3\pi^4 NkT^4}{5\Theta^3} \quad . \quad . \quad (505)$$

From this Debye's law of atomic heats at constant volume follows:

$$c_v = \frac{1}{N}\frac{\partial E}{\partial T} = \frac{12\pi^4 kT^2}{5\Theta^3} \quad . \quad . \quad . \quad (506)$$

For the entropy we get:

$$S = \varPsi + \frac{E}{T} = \frac{4\pi^4 NkT^3}{5\Theta^3} \quad . \quad . \quad . \quad (507)$$

This relation corresponds to Nernst's Heat Theorem, which may be formulated to express its most general meaning in the following way: *the entropy of every body of finite volume which contains exactly similar component parts decreases to an unlimited extent as the temperature decreases to an unlimited extent.*

§ 149. If the body in question is *chemically non-homogeneous,* consisting, say, of N_1, N_2, N_3 . . . atoms of different types, whose sum is:

$$N = N_1 + N_2 + N_3 + \ . \ . \ .$$

we may calculate the characteristic function by following the same course as in § 147. An essential modification occurs only at one point. For as we noticed in connexion with equation (490) we must take into account not only the microscopic states which contributed to the sum of the states there found but also those microscopic states which result from all possible interchanges of the atoms of the body; it was only because the atoms were all assumed to be of the same kind there that this correction did not have to be applied. But if the atoms are, in part, of different kinds an interchange between two atoms of different kinds signifies a new microscopic state and so the sum of the states becomes increased by a new term. As a result of the whole correction we shall get the sum of the states (490) just as many times as there are different permutations among the N atoms. The sum of the states will therefore have to be multiplied by:

$$\frac{N!}{N_1!\,N_2!\,N_3!\,\ldots}$$

or, by Stirling's Theorem (386), by:

$$\left(\frac{N}{N_1}\right)^{N_1}\cdot\left(\frac{N}{N_2}\right)^{N_2}\cdot\ldots=\left(\frac{1}{c_1}\right)^{N_1}\cdot\left(\frac{1}{c_2}\right)^{N_2}\cdot\ldots$$

where the concentrations c_1, c_2 . . . are the same as in (191). Hence we get for the required sum of the states of the body:

$$Z=\left(\frac{1}{c_1}\right)^{N_1}\cdot\left(\frac{1}{c_2}\right)^{N_2}\cdot\ldots e^{-\frac{E_0}{kT}}\cdot\left(1-e^{-\frac{h\nu_1}{kT}}\right)^{-1}\cdot\left(1-e^{-\frac{h\nu_2}{kT}}\right)^{-1}\cdot\ldots$$

and, by (420), for the characteristic function:

$$\Psi=-\frac{E_0}{T}-k\sum_{i=1}^{i=3N}\log\left(1-e^{-\frac{h\nu_i}{kT}}\right)-k\Sigma N_1\log c_1 \quad . \quad (508)$$

an expression which differs from the corresponding expression (491) for a chemically homogeneous body only in having the additional term:

$$-k\Sigma N_1\log c_1. \quad . \quad . \quad . \quad . \quad . \quad (509)$$

This term has no influence on the energy E, because it does not depend on the temperature; but it occurs in the entropy and this is in agreement with the result (190) of the thermodynamic calculation, since $kN=Rn$.

For low temperatures, for example, the entropy of a solid solution becomes by (507):

$$S=\frac{4\pi^4NkT^3}{5\Theta^3}-k\Sigma N_1\log c_1. \quad . \quad . \quad (510)$$

The entropy, then, does not diminish to an unlimited extent as the temperature decreases but approaches the finite value (509).

It is fitting to recall here the general law stated at the end of § 136, that if a body is cooled down sufficiently far all thermodynamic concepts lose their meaning.

§ 150. The knowledge of the absolute value of the characteristic function and the entropy of a body enables us to state completely the conditions of its physical and chemical equilibrium in contact with other substances, whereas general thermodynamics must always leave an undetermined additive constant in the equilibrium formula. As an example we shall apply our results to the equilibrium of a monatomic vapour in contact with its condensate.

By (139) the equilibrium formula runs :

$$\psi - \psi' = \frac{p(v - v')}{T} . \tag{511}$$

where ψ and v are not here to refer to the unit of mass but to the mass of an atom of the gas, while ψ' and v' denote the corresponding quantities for the condensate.

We shall assume the temperature to be so low that in the last equation all those terms may be neglected which decrease without limit as the temperature decreases. If we substitute (474) for ψ, (504) for ψ' and neglect v' in comparison with v we get :

$$k \log \left\{ \frac{ev}{h^3} (2\pi m k T)^{\frac{3}{2}} \right\} - \left(\frac{E_0}{N} - \frac{E'_0}{N'} \right) \cdot \frac{1}{T} = \frac{pv}{T}.$$

Here the constant multiplied by $\frac{1}{T}$ denotes the difference of the zero-point energies of a gaseous and a condensed atom, that is, the heat of vaporization r_0 per atom at the zero of temperature. If instead of the atomic volume v we use (476) to introduce the pressure p, the last equation becomes :

$$k \log \left\{ \frac{ekT}{h^3 p} (2\pi m k T)^{\frac{3}{2}} \right\} - \frac{r_0}{T} = k$$

or, if we now represent p, the pressure of the saturated vapour, as a function of the temperature T we get :

$$\log p = -\frac{r_0}{kT} + \log\left\{\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} (kT)^{\frac{5}{2}}\right\}. \tag{512}$$

We have for the relation between the mass of an atom and a mole :

$$M = \frac{R}{k} m$$

and for the heat of vaporization in calories, by (42) :

$$\lambda_0 = \frac{R}{k}\frac{r_0}{a}$$

Consequently if we measure the pressure in atmospheres, that is, divide p by 1,013,250 and take logs to the base 10 we have :

$$\log p = -\frac{a}{R}\log e \cdot \frac{\lambda_0}{T} + \frac{5}{2}\log T + \frac{3}{2}\log M + \log\left\{\left(\frac{2\pi}{h^2 R}\right)^{\frac{3}{2}} \cdot \frac{k^4}{1013250}\right\}$$

Taking the value of a from (42), R from (55), k and h from (466) we get :

$$\log p = -0{\cdot}219 \cdot \frac{\lambda_0}{T} + 2{\cdot}5 . \log T + 1{\cdot}5 \log M - 1{\cdot}59 \tag{513}$$

This formula agrees with the results of measurement for the pressure of the saturated vapour of monatomic gases in most cases and so remarkably justifies our faith in the assumption that there is an absolute entropy as derived from the quantum theory. In applying it we must note that the numerical value of the chemical constant on the right depends on the units chosen for pressure, temperature and atomic weight. Any deviation of the measured value from the theoretical value must be interpreted in the sense that the atoms are either not all of the same kind or are not invariable. In the first case the constant

(509) becomes added to the expression for the characteristic function; in the second case the equation (471) for the energy of the gas is to be correspondingly generalized, since then not only the kinetic energies of the atomic motions but also other kinds of energy must be taken into consideration.

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